S. Schlorholtz

Refinement of Rapid PCC Coarse Aggregate Testing Program

October 1999

Sponsored by the
Iowa Department of Transportation
Project Development Division

Iowa Department of Transportation

Iowa DOT Project HR-1071

REPORT

IOWA STATE UNIVERSITY
OF SCIENCE AND TECHNOLOGY

Department of Civil and Construction Engineering

The opinions, findings, and conclusions expressed in this publication are those of the author and not necessarily those of the Project Development Division of the Iowa Department of Transportation.

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ABSTRACT

The characterization and categorization of coarse aggregates for use in portland cement concrete (PCC) pavements is a highly refined process at the Iowa Department of Transportation. Over the past ten to fifteen years much effort has been directed at pursuing direct testing schemes to supplement or replace existing physical testing schemes. Direct testing refers to the process of directly measuring the chemical and mineralogical properties of an aggregate and then attempting to correlate those measured properties to historical performance information (i.e., field service record). This is in contrast to indirect measurement techniques, which generally attempt to extrapolate the performance of laboratory test specimens to expected field performance. The purpose of this research project was to investigate and refine the use of direct testing methods, such as X-ray analysis techniques and thermal analysis techniques, to categorize carbonate coarse aggregates for use in portland cement concrete.

The results of this study indicated that the general testing methods that are currently used to obtain data for estimating service life tend to be very reliable and have good to excellent repeatability. Several changes in the current techniques were recommended to enhance the long-term reliability of the carbonate database. These changes can be summarized as follows.

- Limits that are more stringent need to be set on the maximum particle size in the samples subjected to testing. This should help to improve the reliability of all three of the test methods studied during this project.
- X-ray diffraction testing needs to be refined to incorporate the use of an internal standard. This will help to minimize the influence of sample positioning errors and it will also allow for the calculation of the concentration of the various minerals present in the samples.
- Thermal analysis data needs to be corrected for moisture content and clay content prior to calculating the carbonate content of the sample.

INTRODUCTION

The purpose of research project HR-1071 was to investigate and refine the use of direct testing methods, such as X-ray analysis techniques, thermal analysis techniques and pore index measurements, for the categorization of carbonate coarse aggregates. The goal of the project was to ensure that the basic test methods are sound so that they can be used to produce unbiased estimates of how any particular carbonate aggregate will perform in portland cement concrete (PCC) pavements. The purpose of this final report is to document the results of the research project and to make recommendations concerning improvements that can be made in the test methods.

Background and Definition of the Problem

Modern construction practices have evolved considerably during the past fifty years. Today, contractors attempt to maximize throughput and minimize costs. This "fast-track" approach tends to increase efficiency but it can pose some problems. Aggregate acceptance programs, which historically were built on stock piling and physical test methods, have been slow to react to these changes. Large contractors now have the ability to mine, crush and incorporate aggregate into concrete pavement in ever decreasing periods of time. In a modern sense, one could say that aggregate inventory has been minimized to lower risk. Contractors have typically strived to meet the requirements dictated by the appropriate specifications; however, the feed back loop from traditional test methods (measured in days for fast tests, to months for certain durability tests) have been too slow to utilize quality control/quality assurance testing procedures on a routine basis. This fact has stifled innovation. A contractors worst nightmare would probably consist of something like the following scenerio:

> A large paving project reaches completion on time and within budget but with the wrong coarse aggregate in a specific section of the pavement due to a transportation error. A couple of months after the project ends the contractor is informed by the proper authorities that the pavement does not meet the aggregate specifications and must be replaced. Who pays for a job well done but with the wrong aggregate? How much pavement longevity would be lost due to the use of the wrong aggregate?

His basic concept for categorization of carbonate stones has been reproduced in Figure 1. The figure illustrates the simplicity of the model that evolved during Dubberke's 30+ year employment at the Iowa DOT. The key features of the model all relate to pavement service life as measured from field observations of pavements across Iowa. The major decision points use information obtained from the rapid test methods that were the subject of this study. A detailed discussion of the quality number algorithms and calculations was considered to be outside the scope of this report.

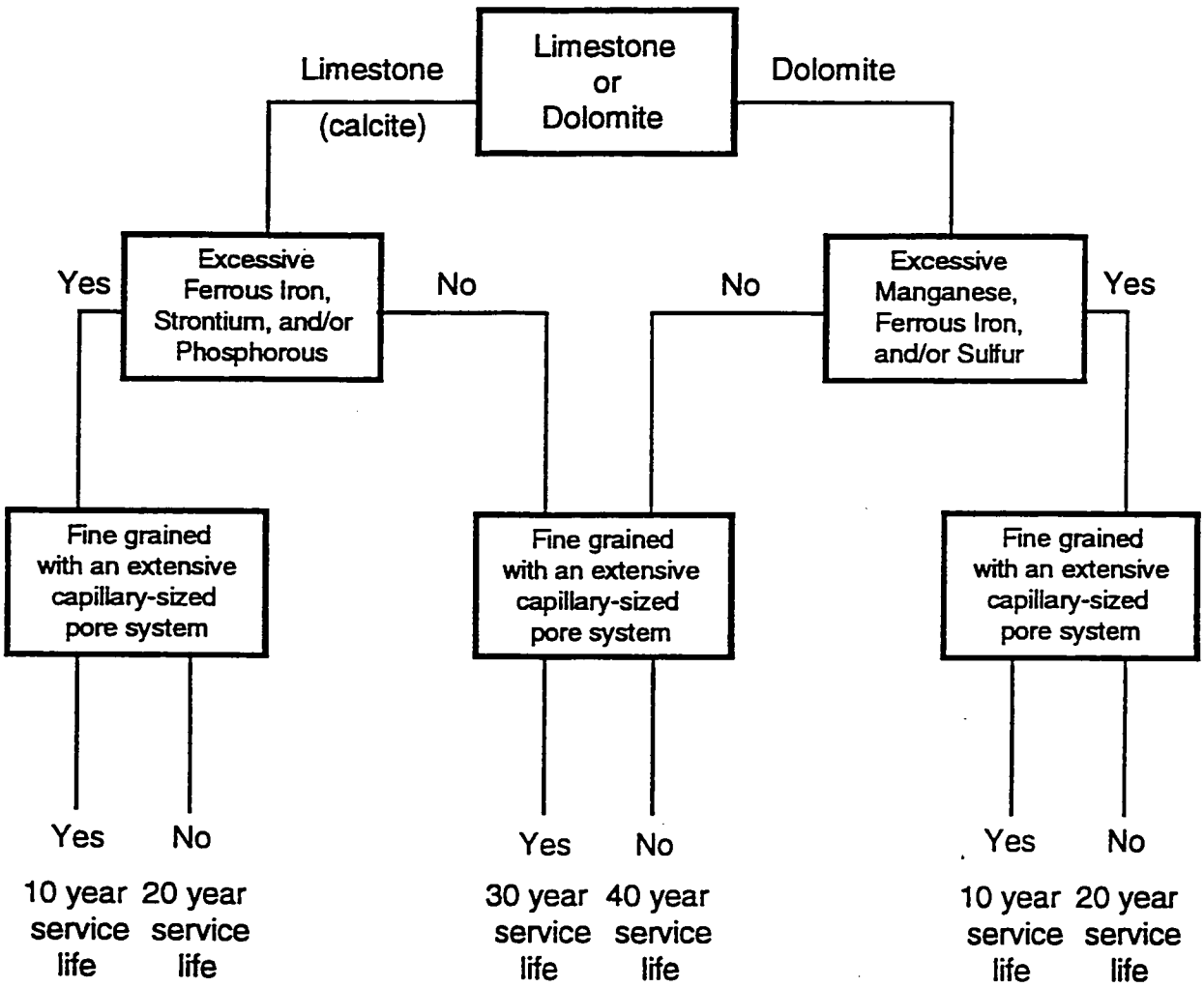


Figure 1. Iowa DOT flow chart for the evaluation of carbonate aggregate.

Previous research by the Iowa Department of Transportation (Iowa DOT) has indicated that direct testing is a simpler, quicker and less expensive method of categorizing aggregates for use in concrete [1]. Also, direct testing has the potential to provide quick information that could be used on a quality control/quality assurance basis to ensure that the proper aggregates are incorporated into any specific concrete pavement. The goal of this research project was to refine the current direct testing methods used by the Iowa DOT. These direct testing techniques form the basis of the creation of aggregate quality numbers.

Aggregate Quality Numbers

A large database was created by Iowa DOT geologists during the past 15 years. The database contains information pertaining to a wide variety of different tests that were routinely conducted on samples of coarse aggregate taken from various quarries across the state. The information includes chemical and mineralogical information, thermal analysis test results, Iowa pore index test results, service life estimates, plus the results from many assorted standard ASTM aggregate tests. Portions of the actual laboratory samples that were analyzed to provide the database information were available for analysis during this project. The goal of Iowa DOT geologists was to create a new aggregate classification scheme that was based only on direct testing methods. The aggregate classification scheme was perceived to be most applicable to portland cement concrete carbonate coarse aggregates that were exposed to liberal application of deicing salts. The combined results of which could be represented by an aggregate quality number. Quality numbers for aggregates typically range from about 0 (very good) to 10 (very poor). The concept of aggregate quality numbers is not entirely new. Larson, et al [2] in 1964, described the possibility of using "index ratings" to categorize aggregates for use in portland cement concrete. Their proposed index rating scheme suggested that the pertinent variables were the physico-chemical properties of the paste and aggregate phases and environmental conditions. In contrast, the procedure described in this report is based on bulk chemistry and mineralogy (X-ray and thermal analysis techniques), and porosity (Iowa pore index test [3]) of only the coarse aggregate.

Much of the aggregate quality number work that was performed by the Iowa DOT was conducted by Wendell Dubberke, retired Iowa DOT geologist.

EXPERIMENTAL METHODS AND EQUIPMENT

A Philips PW 2404 X-ray fluorescence spectrometer was purchased for this project. The spectrometer is equiped with a 167 specimen sample changer (only sixty positions active at this time) and is fully computer controlled. This spectrometer replaced the SIEMENS SRS 200 spectrometer which had been used by Iowa DOT personnel since the early 1980's. A comparison of the features available on the two systems is given in Table 1. The Philips spectrometer uses SUPERQ [4], a Windows 95 based software system that greatly simplifies the use of the spectrometer. Novices can quickly learn how to use the spectrometer to analyze (qualitatively, semi-quantitatively or quantitatively) a wide variety of different materials. The new spectrometer readily accepts solids, semi-solids or liquids in the same sample queue.

Three basic sample preparation strategies were used to collect chemical information about Iowa carbonate stones. The sample preparation methods consisted of the loose powder technique, the pressed pellet technique and the fused disk technique. Standard operating procedures (SOP's) for each of the methods are given in Appendix 1. A limited number of standards were available for calibrating the results obtained from the three methods. Not all standards could be used for each of the sample preparation techniques.

Table 1. Features available on the two X-ray spectrometers.

Item	SIEMENS SRS 200	PHILIPS PW2404
X-ray Tube	Chromium (Cr) Side window	Rhodium (Rh) End window
Generator (max. setting)	2.5 kW	4.0 kW
Analyzing Crystals	6	6
Collimators	2	3
Filters	1	3
Apertures	2	4
Element Range	Na thru U (vacuum)	B thru U (vacuum) Na thru U (Helium path)
Software	DOS (second party vendor), quantitative and some qualitative features	Windows 95 (or NT) Qualitative, semi-quantitative and quantitative features

RESEARCH APPROACH

The thrust of this research project was aimed at verifying the reliability of the direct testing methods that had been developed for testing carbonate coarse aggregates. The tasks that were conducted included: (1) verification of the precision and accuracy of the bulk chemical test methods; (2) creation of a data presentation platform that could be used to view the data; and (3) to compile and analyze the results obtained from the various techniques in an effort to assess the performance of the quality number approach to aggregate quality.

The verification of the bulk chemical testing method was conducted on a subset of approximately 100 samples that were selected to represent the limits of carbonate stones that are normally encountered in Iowa. This assessment was needed because of the replacement of a major piece of equipment that had been used in the test procedure. The subset of samples was analyzed using both the old and the new X-ray spectrometer to see if they generated identical test results. This step was required to maintain the internal consistency of the overall database which contained several thousand records.

The second task, creation of a data presentation platform, was greatly simplified during a meeting of Iowa DOT personnel (Dubberke, Gossman, Narotam and Hanson) and Materials Analysis and Research Laboratory (MARL) personnel (Schlorholtz and Amenson) in February, 1998. During this meeting it was agreed that the MARL would simply make the chemical test results available to the Iowa DOT in a standard format. The Iowa DOT personnel indicated that they would maintain and update the existing database at their own facilities. They would also be responsible for generating aggregate quality numbers.

The final compilation and analysis of the direct testing data and the corresponding quality numbers was performed in conjunction with Iowa DOT personnel (Narotam, Jones, Hanson and especially Dawson and Gossman) at several independent sessions. The meetings were conducted from December 1998 through approximately May, 1999. The results of these collaborative sessions will be documented in detail in a subsequent report.

analysis system, this should greatly simplify data collection, data reduction and the incorporation of test results into the basic calculations needed to generate aggregate quality numbers.

All of the pore index tests conducted for this project were performed at the Iowa DOT by Iowa DOT personnel. The standard apparatus and normal operating procedures were used throughout this study. Previous research has indicated that the Iowa pore index test is a quick and reliable test for categorizing the pore stucture of carbonate stones [3]. Pore structure of carbonate aggregates plays a significant role in field performance. The pore index test is relatively quick and utilizes a large sample size so the method could be developed into a quality control test for carbonate aggregates. The test has undergone extensive evaluation by Iowa DOT personel. No further evaluations of the test were conducted during this project.

RESULTS AND DISCUSSION

X-Ray Fluorescence (XRF)

Comparison of spectrometers

As expected, the analytical performance of the new spectrometer was highly superior to the old spectrometer. This was due to several major improvements that have occurred in the X-ray analysis industry in the past decade. Briefly, the improvements consisted of the development of more robust X-ray tubes (end window design, thinner Be window, higher current loading), closer coupling of the sample to the X-ray source, and the development of better measuring crystals for light elements (i.e., elements with atomic numbers less than 12). Tables 2 and 3 summarize the results obtained during the analysis of Standard Reference Material (SRM) NBS 1a, an argillaceous limestone, using each spectrometer. The new spectrometer greatly enhances the analytical potential available to any given user.

A suite of 92 samples was used to compare the analytical results from the Siemens SRS 200 spectrometer to those that were obtained on the Philips PW 2404 spectrometer. This was done so that the existing database, which contained several thousand records, could simply be appended with new analytical information. Dubberke recommended small adjustments to the Sr, Mn, P and S values stored in the database so that they would be in better

Several additional pieces of equipment were used to prepare the various test specimens prior to presentation to the spectrometer. All samples were ground to a fine particle size using a SPEX shatter box (cat. number 8511). Hardened steel grinding vessels were used throughout this study. A SPEX press (cat. number 3624) and a SPECAP 40mm die set was used to form the pressed pellets. A LECO FX-503 automatic fusion device used to prepare the fused disks that were analyzed during this project.

A SIEMENS D 500 X-ray diffractometer was used throughout this study. The diffractometer was controlled via a microcomputer by using a Materials Data Inc. (MDI) DATABOX and proprietary software [5]. The diffractometer was equipped with a diffracted beam monochromater and medium resolution slits. A copper X-ray tube was used for all diffraction work. The test specimens were presented to the diffractometer as randomly oriented powders via side-loading or back-loading . The specimens were rotated in the X-ray beam throughout the data collection phase of the experiments. Specimens were scanned from 25 to 35 degrees two-theta to collect information from the strongest diffraction peaks for calcite, dolomite, quartz and feldspar(s). Approximately 15 minutes was required for data collection. Data analysis was performed using the SHADOW profile fitting program or the JADE peak search program from MDI [6]. The standard operating procedure for the X-ray diffraction method used in this study is summarized in Appendix 2.

The thermal analysis studies utilized a TA Instruments 2000 thermal analysis system. The system consisted of a TA Hi-Res. TGA 2950 thermogravimetric analyzer module that was controlled via a microcomputer and proprietary software. The Hi-Res. TGA system was equipped with a 16 sample carousel. A typical TGA experiment used the following analytical parameters: (1) a scanning rate of 40 degrees C per minute, resolution = 5; (2) a sample mass of about 55 milligrams; (3) a carbon dioxide atmosphere (purge rate = 100 milliliters per minute); and (4) test specimens were heated from about 100°C to 1000°C in platinum sample pans. The standard operating procedure for thermal analysis testing has not been included in this report because a major hardware and software upgrade is currently in progress. Hence, the standard operating procedure will be documented when the new hardware and software has been installed and is functional. The upgrade will provide a Microsoft Windows style of user interface for the complete thermal

Comparision of sample preparation techniques

The loose powder technique was very quick and simple. The analyst pours 2.5 to 3 grams of sample into a disposable sample cup and then seals the cup with a film that is relatively transparent to X-rays. This process takes less than one minute per sample; and hence, it is deemed most appropriate when large number of samples require analysis. The major drawback of the method is that the samples exhibit poor detection limits for sodium (Na) due to the strong absorption of sodium X-radiation by the film (see Figure 2). Also, the loose powder specimens must be run in a helium path to avoid unnecessary contamination of the spectrometer chamber, this also reduces the intensity of light elements (see Figure 3). However, the effect is much smaller than the influence of the film. The two effects are superimposed on each other and the net result is the loss of about 80% of the intensity from sodium (Na) radiation (see Figure 4). This effect becomes negligible for elements with atomic numbers greater than 20 (i.e., calcium).

The pressed pellet technique was also quite simple and straight forward. It consisted of mixing the sample with a small amount of binder and then pressing the powder at 25 tons of load. This produced a pellet that was very compact and durable. However, the technique does not allow the sample throughput that the loose powder technique provided. Typically it took about 10 minutes to prepare a pressed pellet specimen. The major benefits of the method were that the pellets were very durable and that they could be run in a vacuum. Hence, the pressed pellet technique exhibited the highest analytical sensitivity for light elements of the three methods that were investigated in this study. This fact lends itself to the quick semi-quantitative analysis of carbonate stones for a wide variety of different elements. An application denoted as "Pellet Scan" was created to provide a relatively quick semi-quantitative method for determining the elements present in a pressed pellet specimen. This application scans for all elements from oxygen (O) through uranium (U).

The fused disk technique was by far the most robust sample preparation method that was investigated in this study. It was also the slowest. Briefly, one part of sample was fused with five parts of lithium tetraborate at 1080°C, to produce a glass disk. The glass disk was cooled to room temperature and then placed directly into the spectrometer for analysis. The strengths of the fused disk method include: (1) a high level of

agreement with the new values that were generated from the PW 2404 spectrometer. The major elements were in good agreement and did not require adjustment. These adjustments were documented in a memo from Hanson (dated May 6, 1998). The memo and supporting information have been summarized in Appendix 3.

Table 2. General comparison of spectrometer performance (values in net cps).

element	Siemens SRS 200 Powder (vacuum) **Dubberke method**	Siemens SRS 200 Pellet (vacuum)	Philips PW2404 Powder (He path) **Current method**
Mg	113	268	23,009
Na	7.2	25.3	952
Fe	14,834	15,038	62,841
S	947	1292	8238
Ti	5981	6025	1402
Cl	7.6	60.1	352
Si	8438	11336	82,696
Ca	27,752*	28,426*	564,964
K	14,900	15,671	34,532
P	244	392	2190
Al	2596	3849	27,353
Mn	18	Not meas'd	1862
Sr	5067	Not meas'd	103,000

* = not optimal count rate due to counter nonlinearity

Table 3. Analyte sensitivities for the two spectrometers (values in cps per %).

Constituent (element or oxide)	NBS 1a (mass %)	Siemens SRS 200 Powder (vacuum) **Dubberke method**	Philips PW2404 Powder (He path) **Current method**
MgO	2.19	122	10,506
Na_2O	0.39	65	2441
Fe_2O_3	1.63	9226	38,553
S	0.25	5168	32,952
TiO_2	0.16	37,656	8762
Cl	Not certified	≈ 5000	≈ 13,300
SiO_2	14.11	803	5861
CaO	41.32	688*	13,673
K_2O	0.71	22,071	48,637
P_2O_5	0.15	2613	14,600
Al_2O_3	4.16	925	6575
MnO	0.038	474	49,000
SrO	0.23	22,030	447,826

* = not optimal count rate due to counter nonlinearity

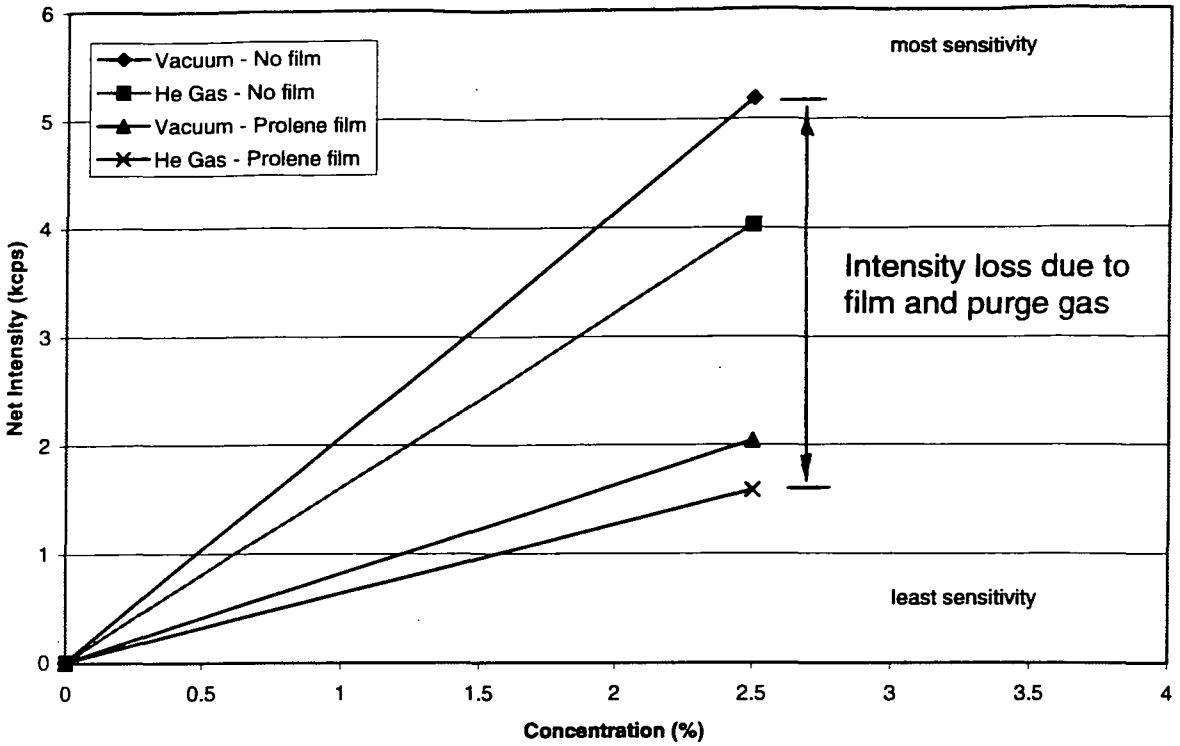


Figure 4. Illustration of loss of sensitivity for sodium (Na) radiation caused by.the support film and the helium purge gas.

both precision and accuracy; (2) standards for the method can be formulated using reagent grade compounds or mixtures composed of different SRM's of widely varing ranges of composition and mineralogy; and (3) interelement corrections and background overlap factors are greatly simplified due to the dilution of the sample with the flux. The method suffers from the fact that it requires highly trained personnel for specimen preparation. It also has rather poor detection limits for light elements and trace elements. The analyst also must be aware of the fact that volatile elements (for example, Cl and S) may leave the specimen during the sample preparation process.

Calibration

The X-ray fluorescence method is a comparative type of analysis. Standards of know composition are used to construct calibration curves that relate the concentration of an element in a sample to the measured X-ray intensity for that element. Then, by measuring the X-ray intensity for any particular element in a sample of unknown composition, the calibration curve can be used to calculate the concentration of that element. The calibration

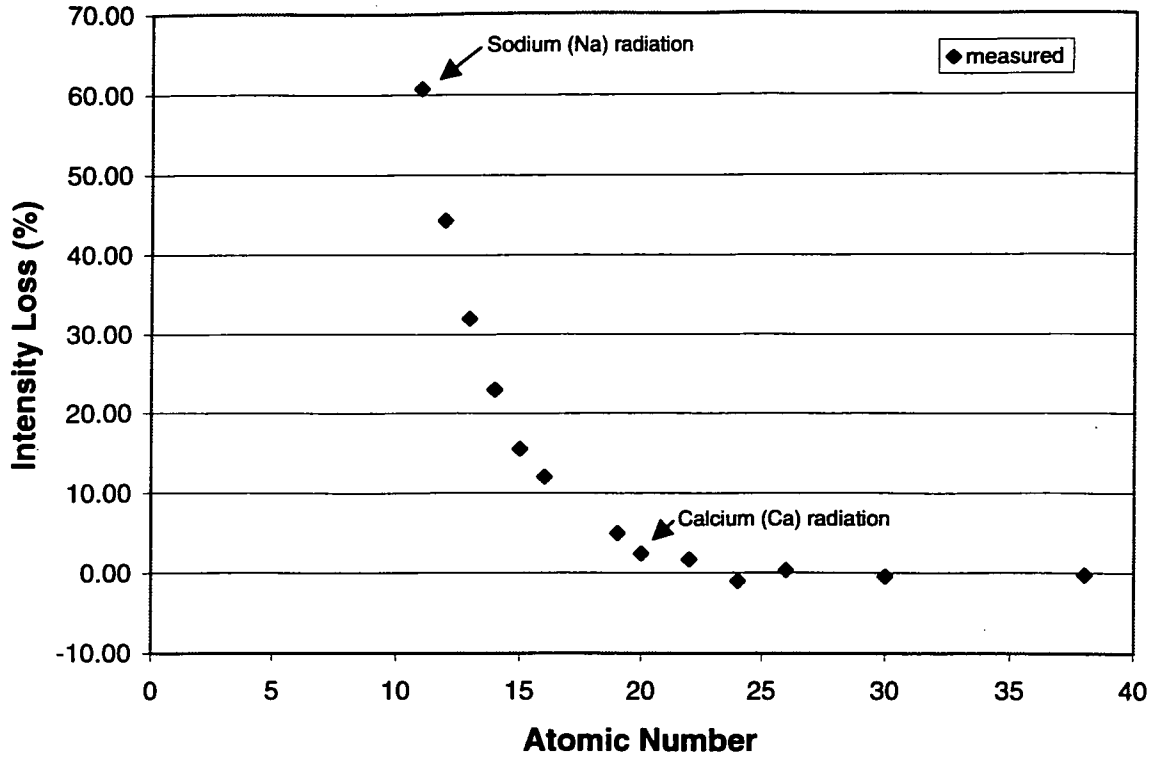


Figure 2. X-ray intensity loss due to support film (PROLENE).

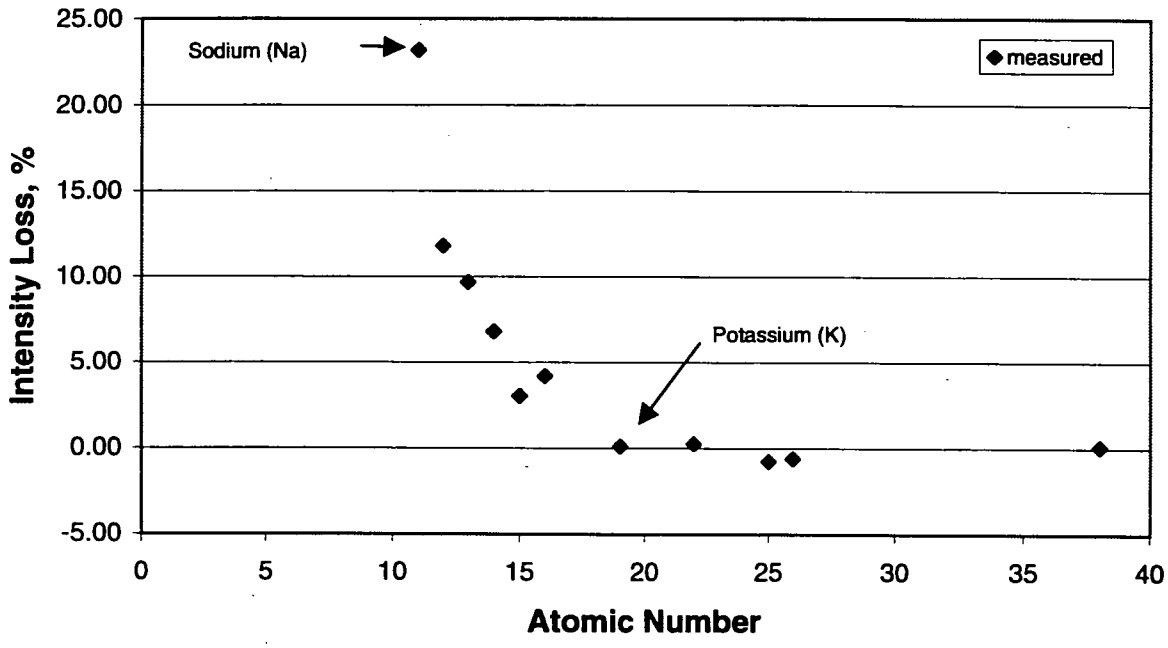


Figure 3. X-ray intensity loss due to helium (He) purge gas.

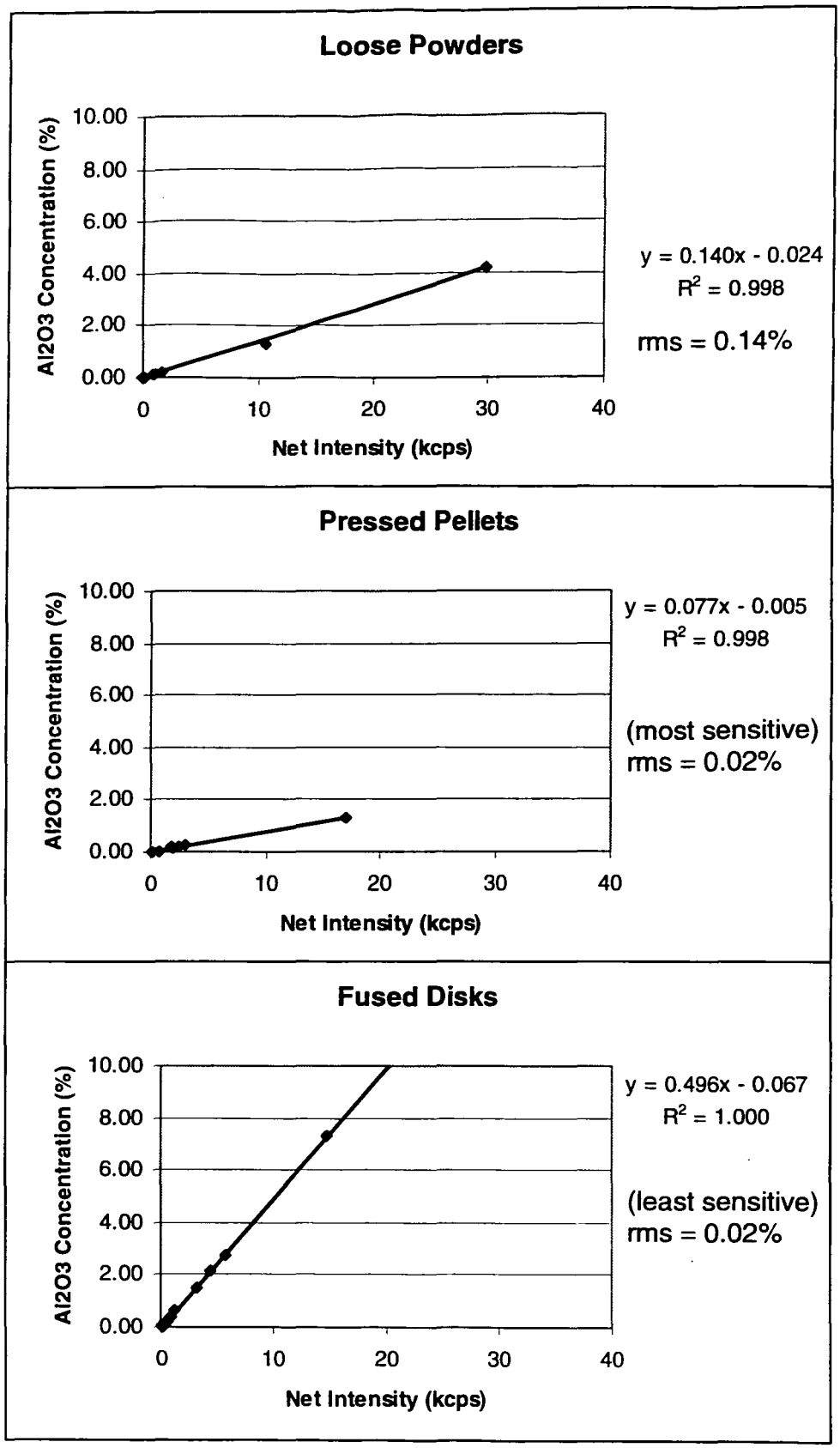


Figure 5. XRF calibration curves for aluminum (expressed as Al_2O_3) for the three different sample preparation techniques used in this study.

curves generated for this study also correct for interelement effects and background overlap factors. These particular features are now simple to employ and they solve many of the analytical difficulties that were documented in a previous report [7].

It is very important to understand that the calibration procedure is most successful when the mineralogy and particle size of the standards are the same as the samples of unknown composition. This places rather severe limitations on the loose powder and pressed pellet techniques because there are only a few good carbonate standards available commercially (see ASTM C 25 [8] for a general summary of the standards that are available). Also, the standards often fail to exhibit the range of composition that is observed in the field samples. Hence, analysts normally turn to mixing standards or adding small amounts of pure compounds to a given standard to expand the ranges of the many elements that are of interest to carbonate geologists. Note, that the fused disk technique is not subject to these limitations because the samples are decomposed into a uniform glass specimen prior to analysis. This allows standards to be formulated to nearly any desired composition.

The calibration process can be rather tedious when the number of elements to be determined or the number of standards to be measured gets large; however, the data collection process is highly automated and modern spectrometer drift correction strategies (which greatly reduce the need for recalibration) help to minimize the effort that is expended. For the sake of brevity, only the calibration curves for aluminum (Al expressed as Al_2O_3) will be discussed in detail. The rest of the calibration curves exhibited similar trends and some of the details have already been discussed in a previous report [7]. All three of the calibration summaries are kept on file at the MARL.

The calibration curves for aluminum (Al) that were obtained from the three different sample preparation techniques are shown in Figure 5. The figure has been constructed using a constant scale so that certain features of the curves can be compared on a uniform basis. First, the slope of each line indicates the sensitivity of the spectrometer to the analyte (Al in this instance). It is apparent that the pressed pellet specimens exhibited the highest sensitivity to Al of the three techniques that were used in this study. The loose powder technique provided the second highest sensitivity for Al, followed by the fused disk technique. Remember that the fused disk technique employs a dilution factor of five (1 part sample to 5 parts flux) so

Table 4. Repeatability of the loose powder sample preparation method.

Element	Carbonate run monitor Mean value (n=20) (mass %)	RMS Error (standard deviation)	Coefficient of Variation (%)
MgO	0.63	0.016	2.6
Na_2O	0.61	0.022	3.7
Fe_2O_3	1.18	0.034	2.9
S	0.25	0.008	3.1
TiO_2	0.16	0.004	2.4
Cl	1.19	0.036	3.0
SiO_2	4.36	0.116	2.7
CaO	46.94	0.641	1.4
K_2O	0.70	0.013	1.8
P_2O_5	0.18	0.006	3.2
Al_2O_3	1.90	0.063	3.3
MnO	0.02	0.000	1.2
SrO	0.07	0.002	2.2

Chemical shift measurements

Geologists often like to know the valence of the atoms that are present in any given sample. An application denoted as "Chem Shift" was created to determine the valence of sulfur in the carbonate rock specimens. Other elements, such as aluminum, silicon and phosphorous to name a few, would also lend themselves to such measurements. The determination is based on the fact that the peak position of the sulfur K-alpha X-ray emission line is very sensitive to the way it is bonded in the solid phase (see Figure 6). Hence, a slow scan over the sulfur peak can be used to determine the valence state of the sulfur atoms. Since mixtures often occur in nature the method was evaluated by placing known amounts of pyrite and calcium sulfate in a calcite standard. The calcite standard was nearly pure so the effects of the addition illustrate the influence of mixed valence states of sulfur in a single specimen (see Fig. 7). The results indicated that the peak movement was still sensitive to valence state and the peak profile could be used to determine the sulfide-sulfate ratio. Deconvolution of the peak was typically necessary to obtain reliable estimates of the sulfide-sulfate ratios; however, other measurement strategies could be investigated in future studies. The preliminary tests that were conducted on carbonate stone samples for this study nearly always indicated that sulfide sulfur (most probably pyrite) was

these results are not surprising. Secondly, the intercept of each calibration curve is a very small number (nearly 0.00%). This allows the Al estimates to be reliable to very low concentrations. And finally, the error in predicting Al_2O_3 content by measuring the intensity of Al X-radiation is also given in the figure. The error listed is the root mean square error and it is apparent that the loose powder technique is the least accurate of the three specimen preparation techniques. The fused disk and pressed pellet techniques exhibited similar levels of accuracy. However, it is important to realize that the calibration standards used to calibrate the pressed pellet technique were restricted to concentrations ranging from about 0% to 1.3% (expressed as Al_2O_3). The fused disk method produced nearly the same accuracy over an Al_2O_3 range from about 0% to 12%. The fused disk technique was easily the most reliable and robust specimen preparation method that was examined during this study. However, accuracy was not the chief concern of this project. Instead, simplicity and speed were the major concerns and only the loose powder technique met these requirements. The analyst always has the ability to use one of the other specimen preparation techniques if higher accuracy is needed.

Repeatability of the loose powder method

The repeatabilty of the loose powder method was evaluated over the course of three months of analyzing routine samples. The repeatability was determined on a single sample (denoted as the carbonate run monitor) that was included in the sample queue during the periodic XRF measurements that were performed by Iowa DOT staff. The results obtained from twenty (n=20) measurements of the carbonate run monitor are summarized in Table 4. Overall, the major elements were reproducible to better than 2% (relative error), while minor and trace elements were reproducible to about 4% (relative error). Some elements did considerably better than these values (for example see the results for Sr, K and Mn). These numbers reflect the "normal" precision that can be expected from the loose powder sample preparation method. The repeatability appears to be limited by packing problems that are inate to the loose powder technique. However, the repeatability appears to be adequate for most of the elements that were included in the study.

the predominant form of sulfur. This was in good agreement with earlier studies [7, 9] which used acid digestion and X-ray diffraction to document the composition of the insolubles present in Iowa carbonate stones.

X-ray Diffraction (XRD)

The goal of an X-ray diffraction experiment is to define the major and minor crystalline phases in a sample. The data can also be used to evaluate the extent of solid solution in the the dolomite crystal structure. Previous research [7, 10] has indicated that the method is quite useful as a diagnostic aid for evaluating aggregate quality. The typical scan range that is used by Iowa DOT personnel is from 25 to 35 degrees two-theta, this covers the compounds illustrated in Figure 8. Hence, an X-ray diffraction experiment produces two numerical measures for each mineral phase present in the sample. Namely, the location of the peak and the size of the peak. The size of the peak, commonly expressed as an integrated intensity or peak area, is proportional to the concentration of the mineral in the bulk sample. The peak position of a given mineral phase is very sensitive to solid solution in the crystal lattice and this is why the method is considered diagnostic for dolomite quality (see Fig. 9). However, some constraints need to be placed on the interpretation of some of the X-ray diffraction measurements summarized in the database. This is necessary because of some errors have apparently crept into the database over the years. For instance, quartz (α-SiO_2) is a mineral that is commonly found in carbonate rocks. Quartz commonly does not exhibit much of a tendency for solid solution so the position of the major peak for quartz should remain relatively constant in the diffraction data. The theoretical peak position for quartz is 26.65° two-theta (equivalent to a d-spacing of 3.342 angstroms but expressed in terms of the measurement process) and the observed distribution for the quartz peak postion is illustrated in the upper half of Figure 10. It is apparent that the peak can shift well over ±0.05° two-theta from the mean position (range of about 0.18° two-theta) and this is an area of concern because the difference between "good" and "bad" dolomite is only about 0.2° two-theta (refer to Fig. 9).

Historically, the Iowa DOT diffraction data was monitored for errors by using Baddeleyite (ZrO_2) as a standard but the actual details of the correction procedure are rather sketchy. A more systematic error correction procedure will be recommended later in this report. The error in the Baddeleyite sample

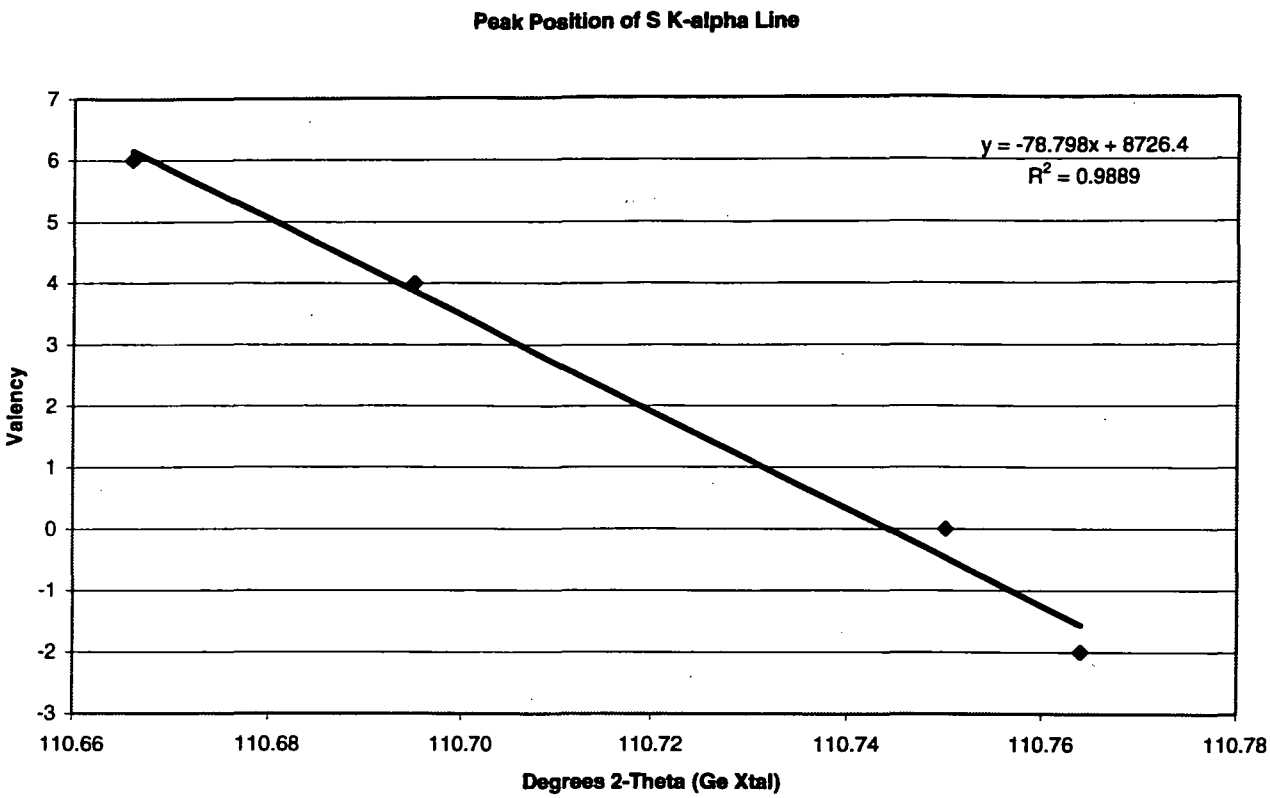


Figure 6. Influence of oxidation state of sulfur on the XRF peak position.

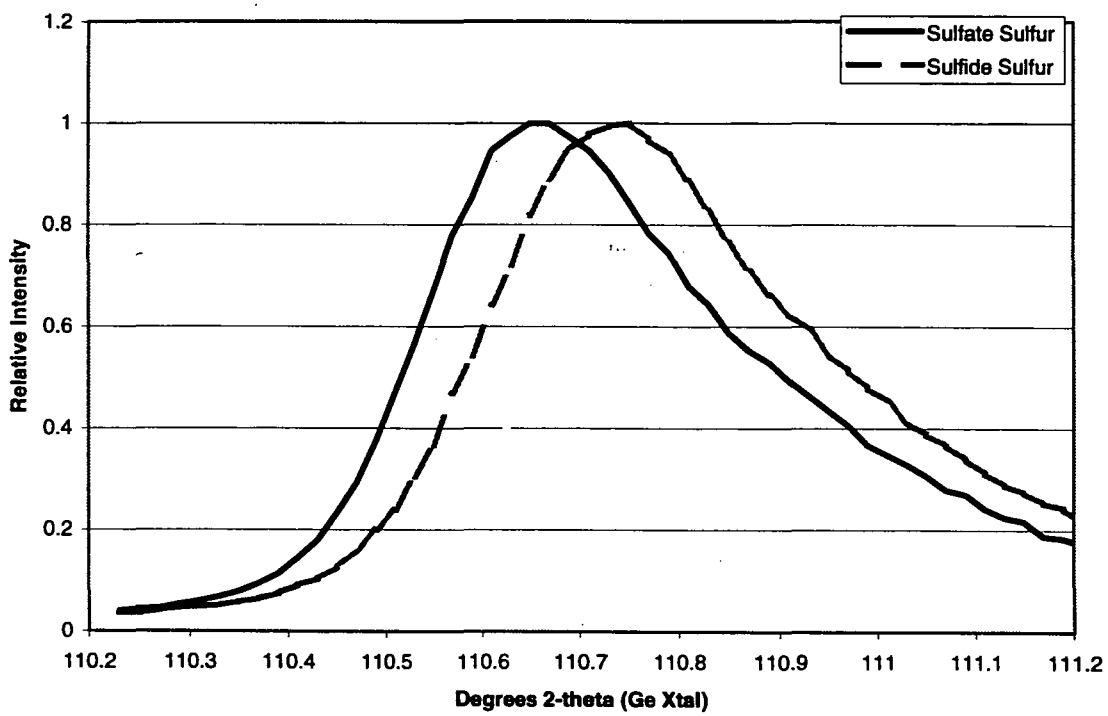


Figure 7. Peak shift of the sulfur K-alpha line for sulfate-sulfur versus sulfide-sulfur in a synthetic carbonate rock sample.

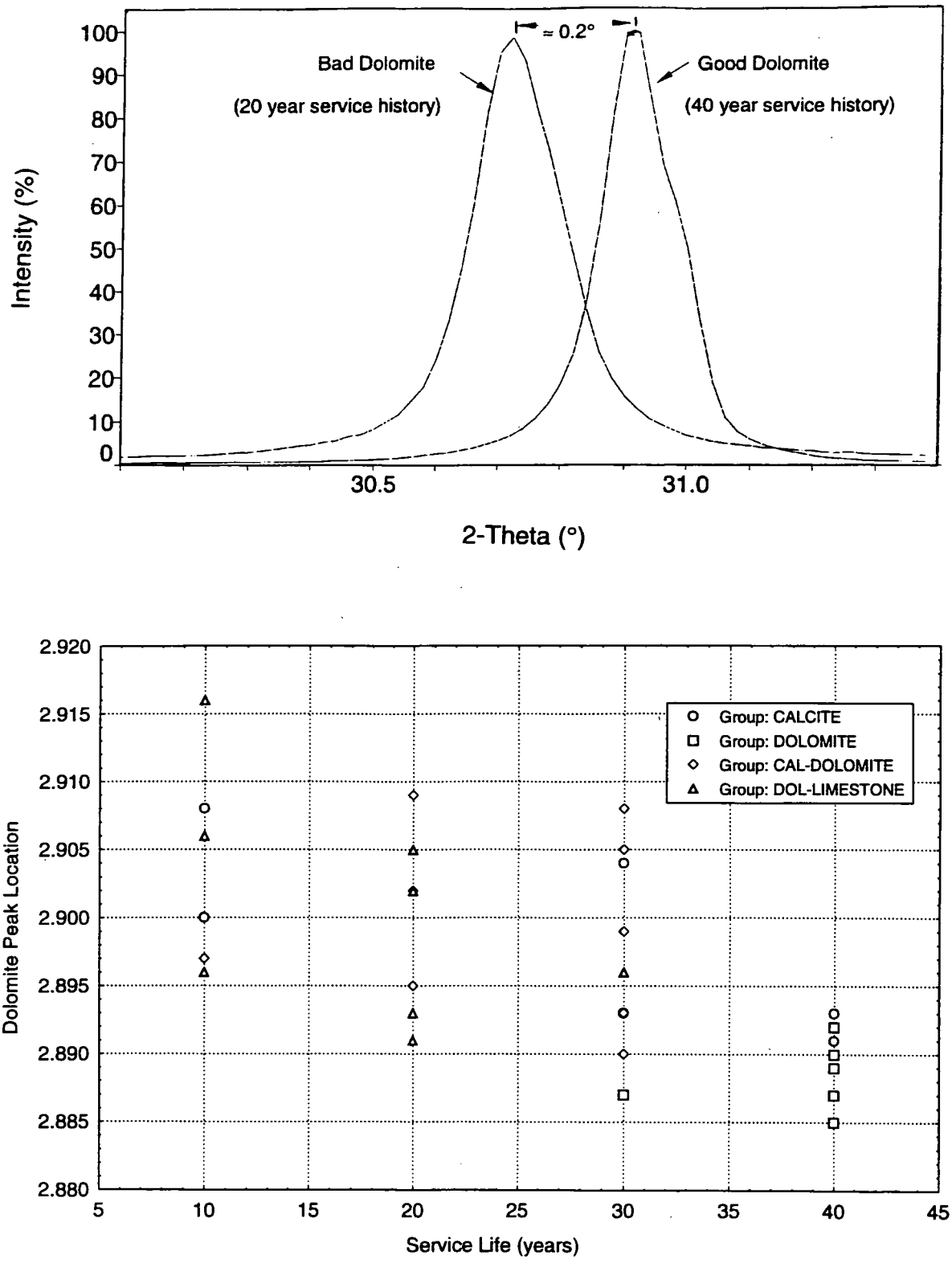


Figure 9. X-ray diffractogram illustrating the peak shift observed for Dolomite-bearing carbonate rocks. Bottom half of the figure illustrates the relationship between service life and peak location.

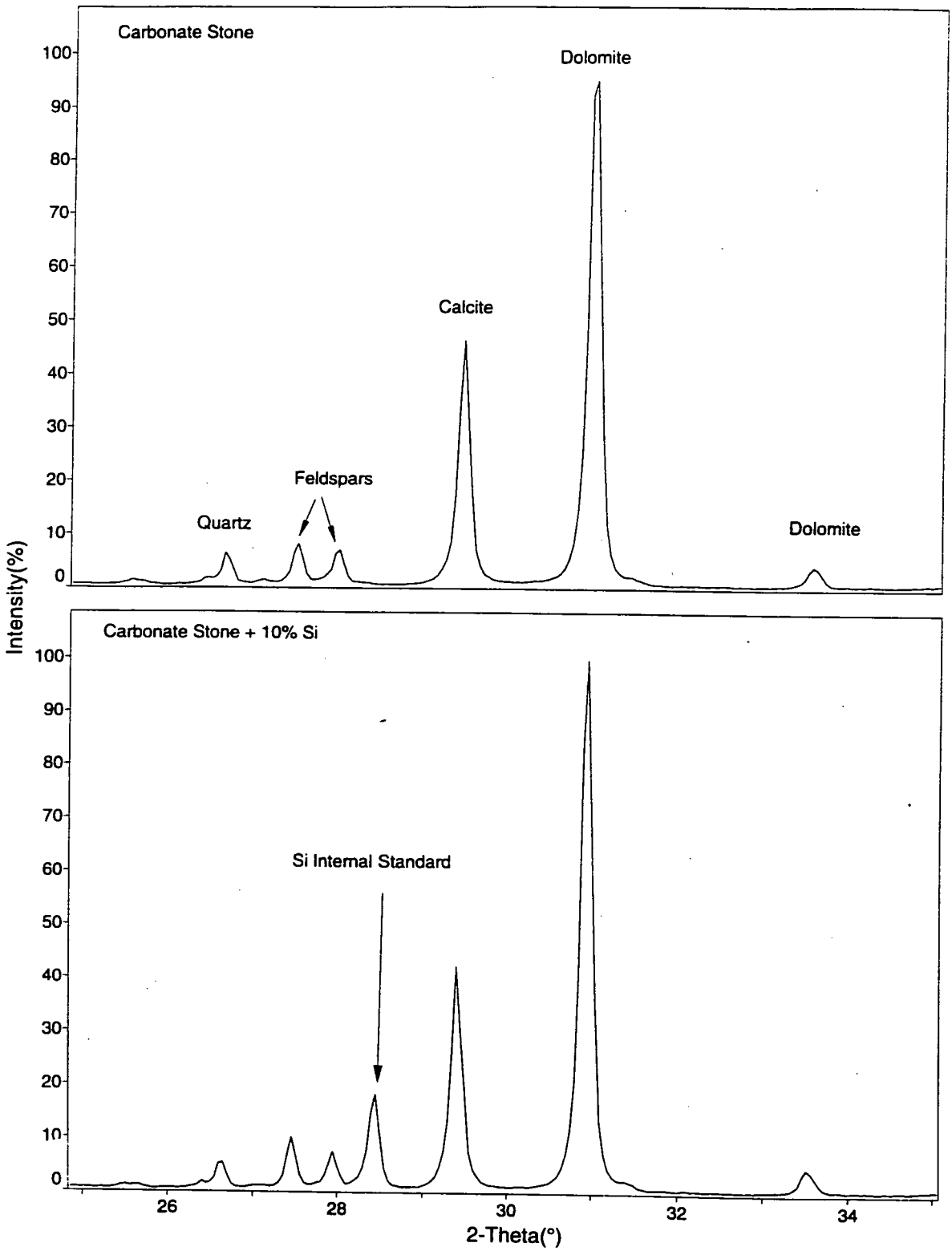
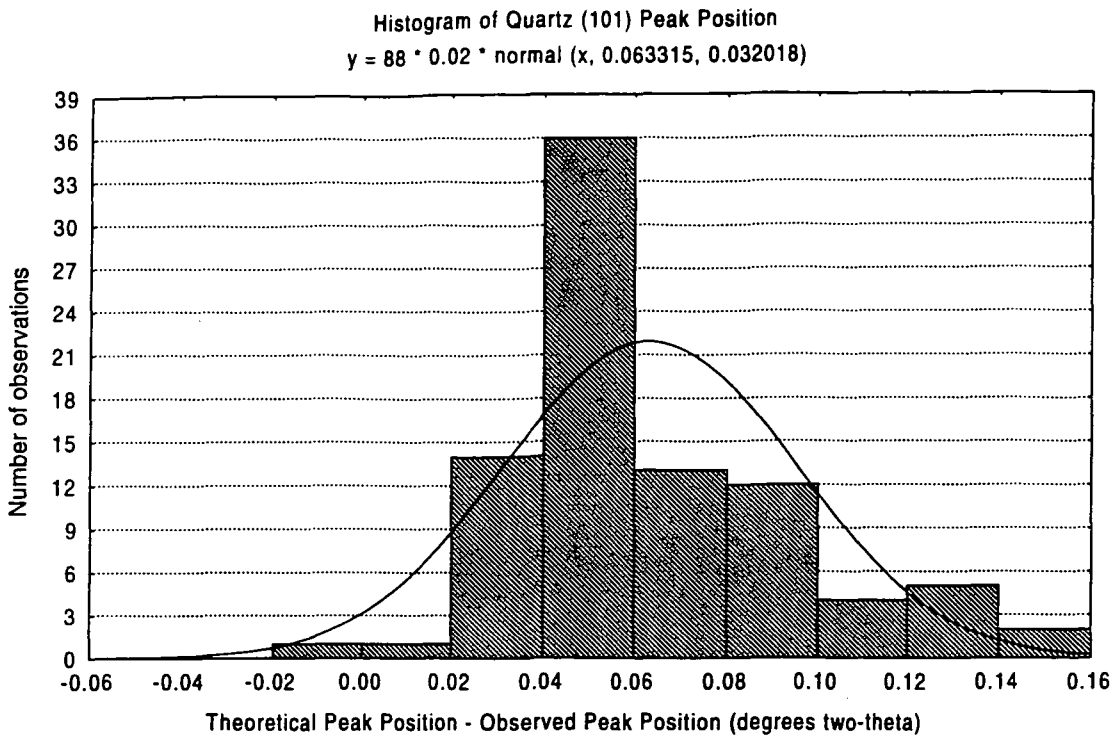


Figure 8. X-ray diffractogram illustrating the major minerals commonly observed in a typical diffraction experiment. Bottom half of figure illustrates the use of silicon as an internal standard.



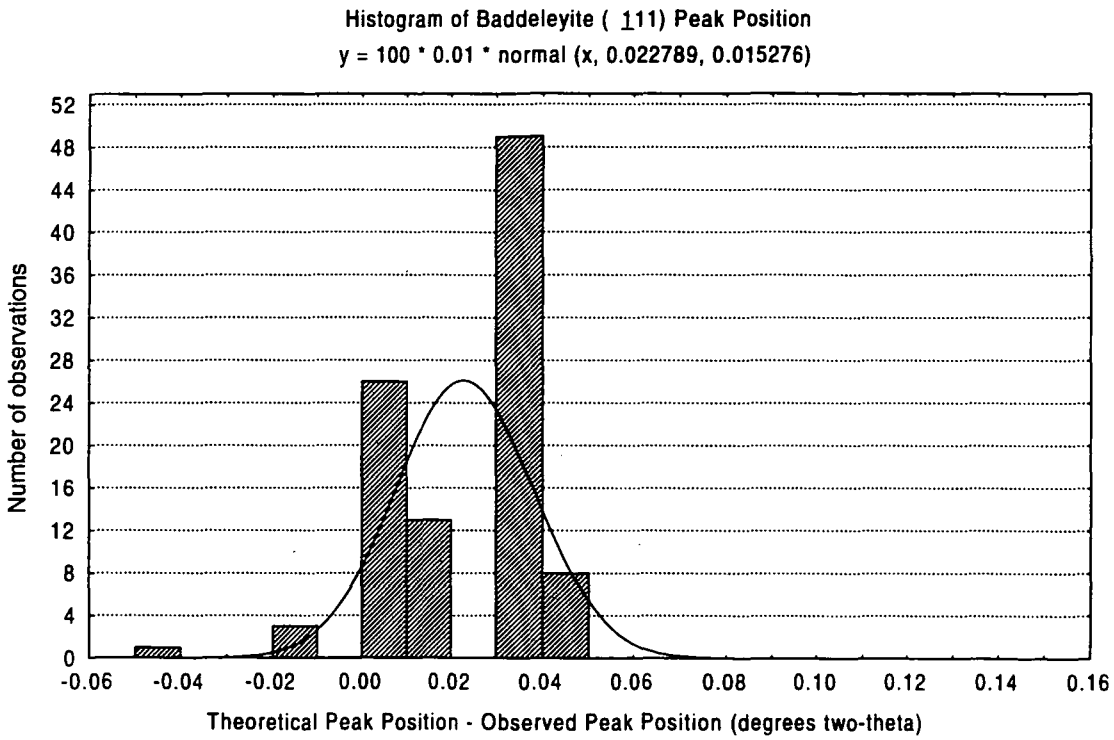


Figure 10. Histograms illustrating peak position errors for minerals in the Iowa DOT diffraction database. Top half of figure shows the data for the (101) Quartz line. Bottom half of figure shows the data for the (1̲11) Baddeleyite line.

(or Baddeleyite + carbonate rock sample) measurements was considerably less than that which was observed for the quartz peak (see the lower half of Figure 10, note that two different sample holders were used to collect the measurements). The observed range was only about half of that which was observed for the quartz peak. These two observations are not consistent and suggest that some discrepancies have crept into the database.

X-ray diffraction measurements commonly suffer from several types of errors. The errors can be corrected by using appropriate measurement strategies or correction procedures. These corrections become relevant to this study because the individual measurements, which we desire to compare to one another to evaluate "quality", have been conducted over relatively long periods of time (i.e., years). Alignment errors and sample positioning errors were the two most common errors present in the X-ray diffraction results for this study. Both errors pertain to the location of any given peak in a diffractogram.

The alignment errors result from the fact that the goiniometer (the part of a diffractometer which measures the angles during an experiment) is a mechanical device that needs periodic adjustment. This adjustment is performed every year or so. However, between adjustments the measured peak position of a standard specimen drifts measurably (see Fig. 11). This drift produces a systematic error in all of the data that is collected using that particular apparatus. The systematic error can be corrected using the external standard method, the internal standard method or by simply aligning the diffractometer more frequently.

The external standard correction procedure utilizes a standard to correct for the systematic peak shift due to misalignment (i.e., very similar to the drift curve shown in Figure 11). The internal standard method is similar to the external standard method except that the standard is mixed directly with each sample prior to analysis. The last option, more frequent alignment of the diffractometer, is not a very realistic option. This is because the process is rather tedious and must only be performed by an experienced professional technician who has been trained to work with equipment that produces X-rays.

The second type of error, a sample positioning error, occurs nearly every time a specimen is subjected to X-ray diffraction analysis. A sample positioning error occurs when the sample surface is not exactly

identical to the initial sample (compare top and bottom halves of Fig. 8); however, peak positions can now be measured with very high accuracy relative to the location of the standard peak. This process is analogous to the use of benchmarks in surveying. Implementation of such a correction technique would minimize discrepancies in the overall carbonate database. It would also allow one to make reliable quantitative estimates of the various minerals observed in the diffraction data.

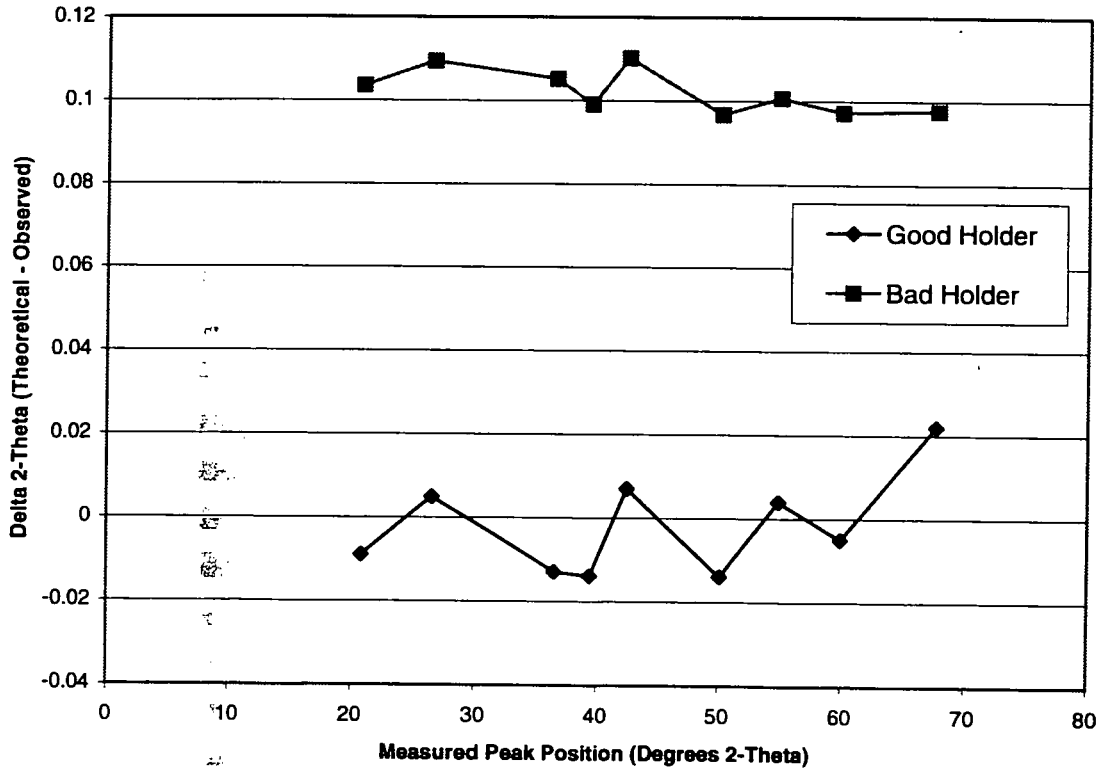


Figure 12. Specimen holder error in X-ray diffractogram measurements.

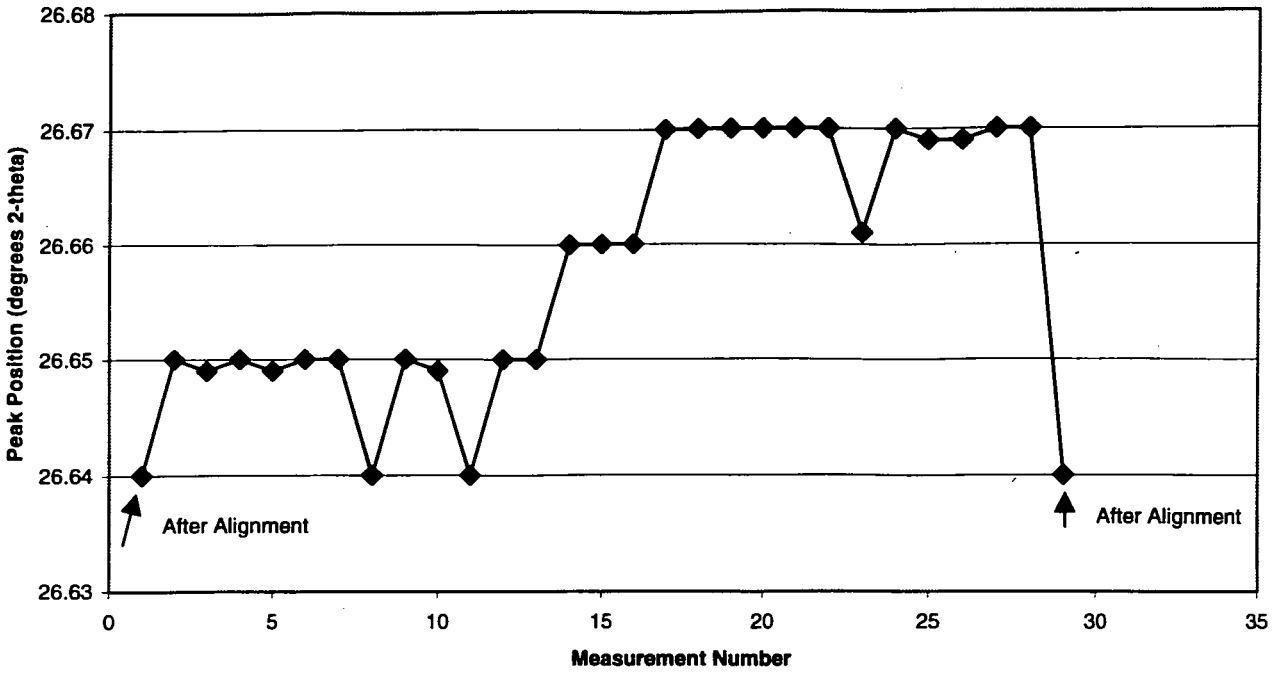


Figure 11. X-ray diffractometer alignment drift.

coincident with the focusing circle of the diffractometer. This displacement can be caused by an error in the specimen holder (a systematic error) or it can be due to the fact that the surface of the powder sample is slightly above or below the reference surface of the specimen holder (a random error because it changes with each specimen). Since diffractometers are aligned to very precise tolerances these errors are easily measurable. An example of a specimen displacement error is illustrated in Figure 12. This particular specimen holder was manufactured with a slight imperfection and produces a systematic error in the peak positions measured for any given sample. This systematic error would disappear if the analyst selected a specimen holder that had been manufactured properly. However, the random error present in the measurement would still remain because of the difficulty of preparing a perfect sample surface for every test.

Of the three correction techniques that have been discussed only the internal standard method has the ability to correct for all the errors that could be present during any arbitrary X-ray diffraction test. With the appropriate selection of a suitable internal standard the final diffractogram remains nearly

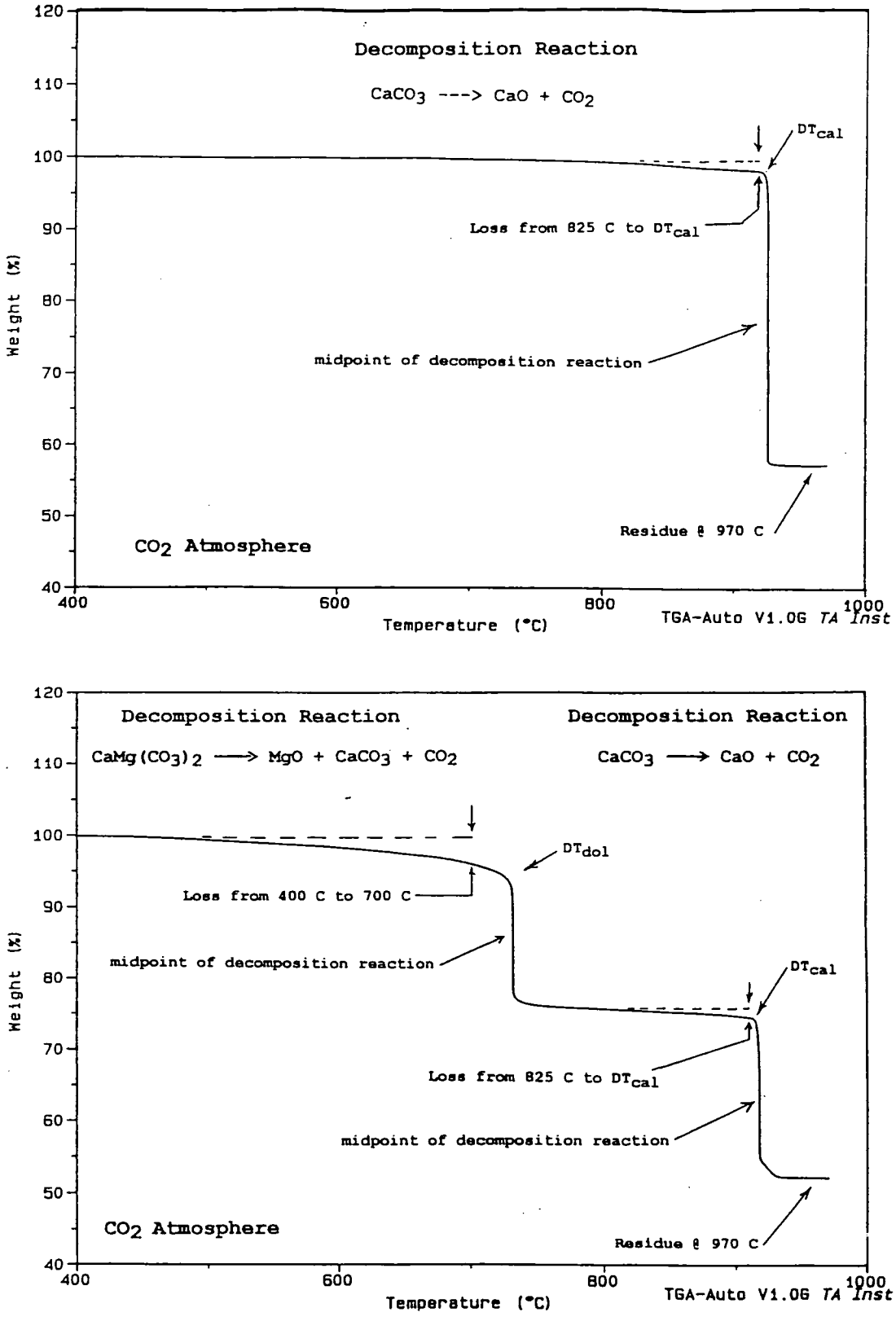


Figure 13. Thermal curves (TGA) observed for carbonate rocks. Top half of figure illustrates a Calcite (limestone) sample. Bottom half of figure illustrates a Dolomite sample.

Thermal Analysis

Thermogravimetric analysis (TGA or TG) has been used extensively for classifying carbonate aggregates [11, 12, 13]. The typical features observed in a TGA test are illustrated in Figure 13. Note the drastic difference between the dolomite and calcite samples, this makes the technique highly diagnostic. The ideality of the themal curves makes data reduction simple and straight forward. Nearly all samples can be successfully analyzed using the autoanalysis program supplied by TA-Instruments [14]. User intervention is only required when the program fails to provide a reliable solution to the thermal curve. This is quite obvious from a visual inspection of the thermal curve.

For the most part the results from TGA testing are very reliable. The method exhibits excellent precision and accuracy, this has been documented in earlier work [7]. However, two sources of error are common enough that they merit discussion. One of the errors is due to inadequate sample preparation (i.e., a particle size effect), while the other is an error that is made during the interpretation of the test results. The second error is commonly associated with the presence of clay minerals (or any other mineral that exhibits a mass loss during a TGA experiment) in the carbonate rock. In most instances, the error associated with ignoring the moisture content and clay content of a carbonate stone is small because of the carbonate decomposition reactions dominate the thermal curves. However, as will be shown later in this section, the error is very measurable when the clay content exceeds approximately 2%.

Previous TGA work at this lab has indicated that the particle size of a sample has a dramatic influence on the test results [7]. This is in good agreement with results reported by other researchers [see references 21 through 26 in [7]]. This error becomes severe when coarse-grained dolomites are analyzed. Figure 14 illustrates the results of a typical TGA experiment on a sample of coarse-grained dolomite (Lamont dolomite). The sample had been ground for two minutes in a shatterbox (a very typical grinding time used for carbonate rocks). The thermal curve indicates that the sample begins to decompose at approximately 400°C. This is much too low of a decomposition temperature for dolomite because X-ray studies have indicated that the value is closer to 530°C [15]. However, closer inspection (see the lower half of Fig. 14) indicates that the decomposition is erratic (bounces the microbalance) and

this suggests that the sample particles have jumped off the sample pan during the experiment. This can cause a major error (about 25% absolute) in the residue determination (i.e., the mass left at 970°C). Since the residue value is often used to estimate the loss-on-ignition (LOI) of the sample this can cause a major discrepancy in LOI's calclulated for coarse grain dolomites. Accurate LOI values are needed to check the overall total of the XRF assays and they can also be used to estimate the acid insoluble residue for limestones.

Clay minerals can complicate the interpretation of the thermal curves of carbonate rocks because they decompose in the same temperature region as the carbonate minerals. This causes overlap in the decomposition profiles that are measured with thermal analysis. Hence, the general calculations that were summarized in a previous report need some modification prior to being applied to clay-bearing carbonate stones. The modification is not simple because clay minerals consist roughly of three major groups and each group exhibits a different thermal decomposition curve. Since all three of the major clay mineral groups (or combinations of the groups) have been identified in carbonate stones common to Iowa [7, 9], it is difficult to formulate an exact solution to the problem. Hence, assumptions need to be made prior to formulating an approximate solution to the problem. Note, that the particle size error must be eliminated prior to even considering an attempt at refining the approximation of the carbonate content of any given sample. This is because the error due to particle size problems greatly exceeds the error due to moderate clay contents (say less than about 10%).

A series of six synthetic standards were made to study the influence of clay content on the decompostion profiles of carbonate rocks. A limestone (Alden) and a dolomite (Lamont) were used to represent nearly "ideal" carbonate rocks. Each sample contained only small concentrations of aluminum and this suggested that they were nearly free of clays. A clay mineral standard (NBS 97a, predominatly composed of a kaolinite clay mineral) was then interground with the Alden and Lamont samples to produce the synthetic standards summarized in Table 5. The samples were then subjected to thermal analysis (TGA) using the procedure described earlier in this report.

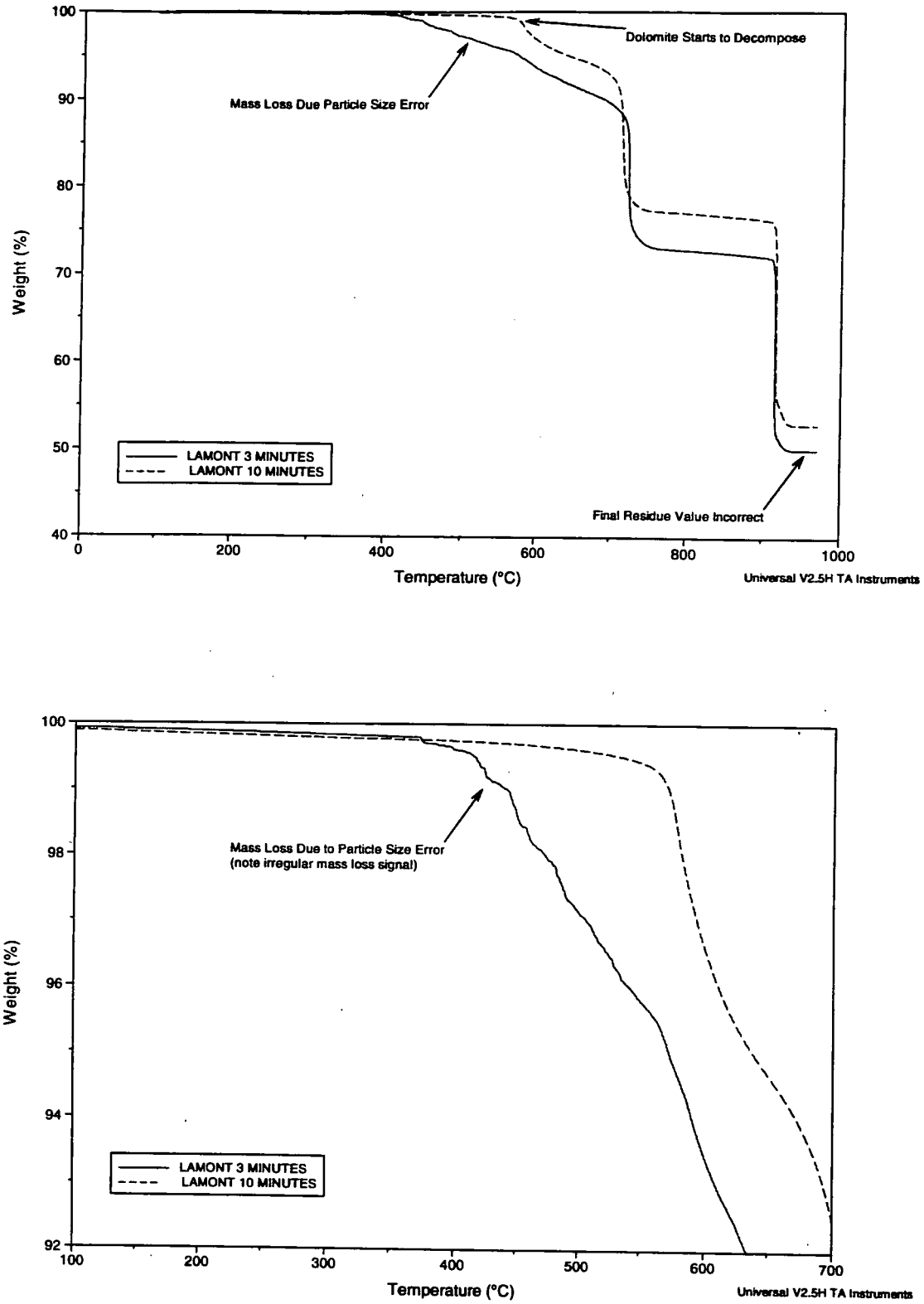


Figure 14. Illustration of the particle size effect that is sometimes observed in the thermal curves of carbonate rocks. Bottom half of the figure expands the y-axis of the thermal curve.

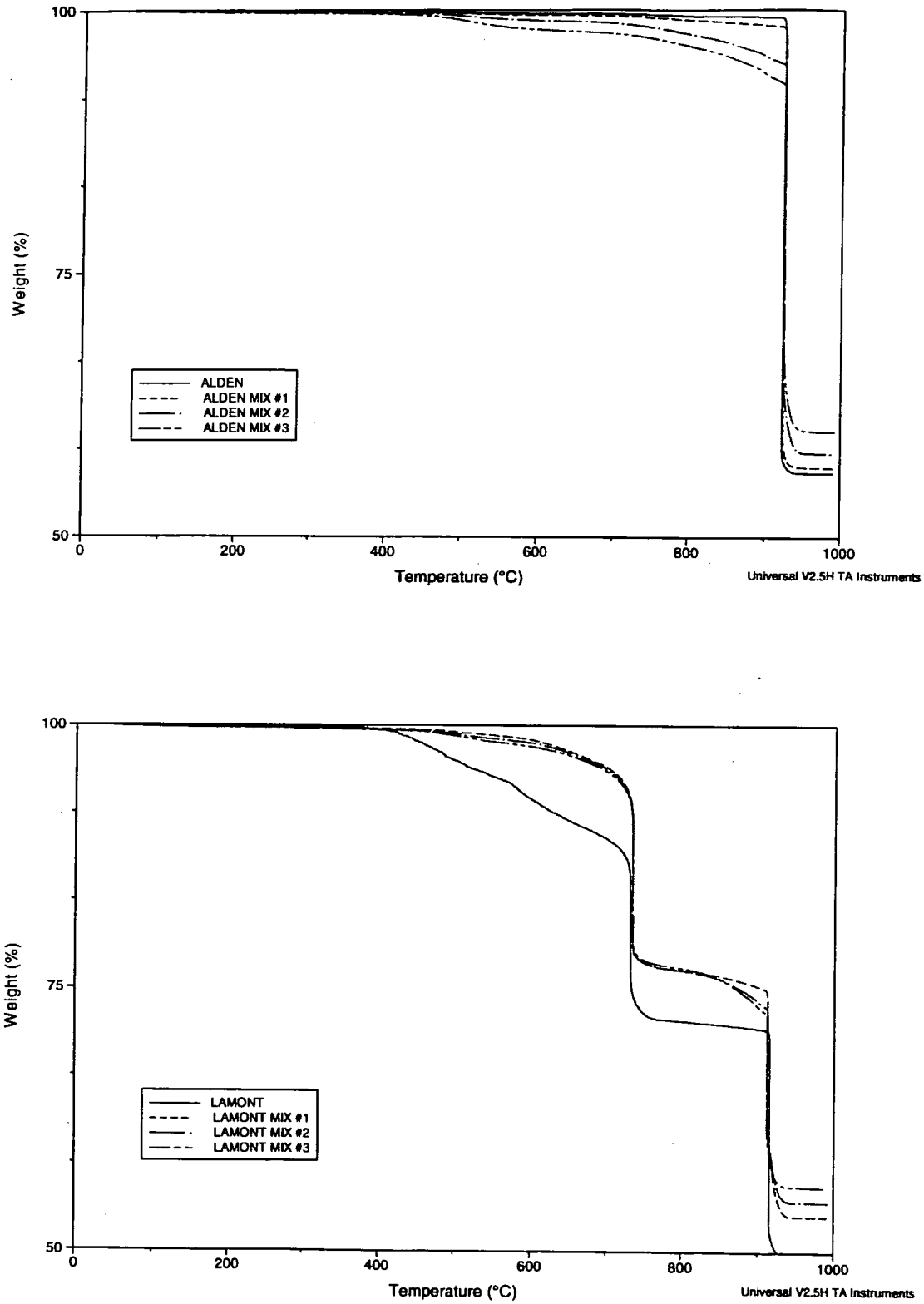


Figure 15. Thermal curves (TGA) for the synthetic standards. Top half of figure illustrates a Calcite (limestone) sample. Bottom half of figure illustrates a Dolomite sample.

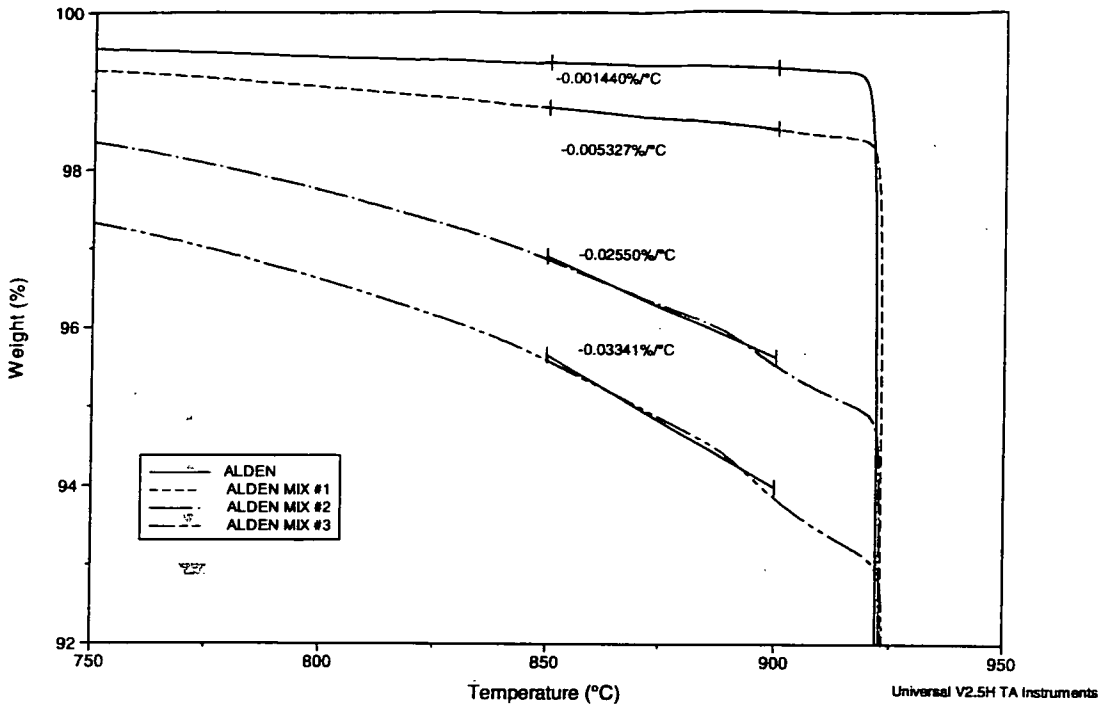
Table 5. Synthetic standards for evaluating clay content.

Sample Name	% Clay Added	Measured % Al_2O_3	Moisture Content, % (loss@150°C)	% Loss from 150°C to 500°C	Slope from 850°C to 900°C
Lamont	0.0	0.26	0.11	Not reliable	-0.0078
Lamont+Mix1	1.7	0.82	0.19	0.64	-0.0197
Lamont+Mix2	5.3	2.21	0.22	0.84	-0.0421
Lamont+Mix3	10.0	3.52	0.24	1.00	-0.0528
Alden	0.0	0.08	0.01	0.24	-0.0014
Alden+Mix1	1.7	0.48	0.14	0.35	-0.0053
Alden+Mix2	5.3	1.87	0.16	0.58	-0.0255
Alden+Mix3	10.0	3.20	0.21	0.99	-0.0334

The results of the thermal analysis tests are shown in Figures 15, 16 and 17. The top half of each figure pertains to limestone (Alden) samples while the bottom half refers to dolomite (Lamont) samples. Specific details, such as weight loss and slope, have also been summarized in Table 5. It is important to keep in mind that the test results only illustrate the behavior of the "ideal" endmembers of carbonate rocks. In practice it is much more typical to have mixtures of limestone and dolomite in a single sample. However, the behavior of such mixtures can be approximated using the results obtained from the current study.

Figure 15 depicts the overall thermal curves that were obtained from the eight different samples. The particle size problem with the coarse grained dolomite sample is very evident in the bottom half of the figure. The figure also gives a gross overview of how clay influences the thermal curves of limestone and dolomite.

Figure 16 is a magnified view of the major clay decomposition region shown in Figure 15. The clay decomposition event becomes very apparent at about the 5% concentration level. At lower clay concentrations the decomposition event is very subtle (especially in the dolomite sample) but it is still measurable (refer to Table 5). This suggests that more work needs to be done on the dolomite samples because of overlapping decomposition events. In contrast, the calcite behaved more uniformly. Note, that the clay decomposition reaction was finished by about 750°C. Figure 17 shows how



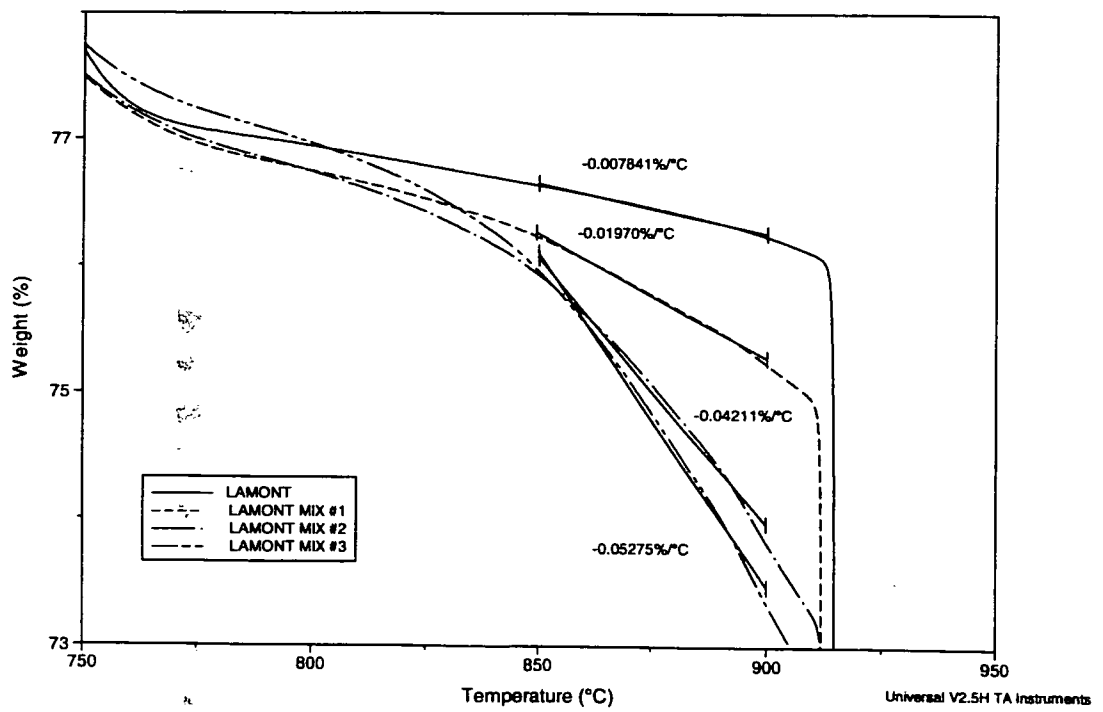


Figure 17. Slopes prior to calcite decomposition for the synthetic standards. Top half of figure illustrates a Calcite (limestone) sample. Bottom half of figure illustrates a Dolomite sample.

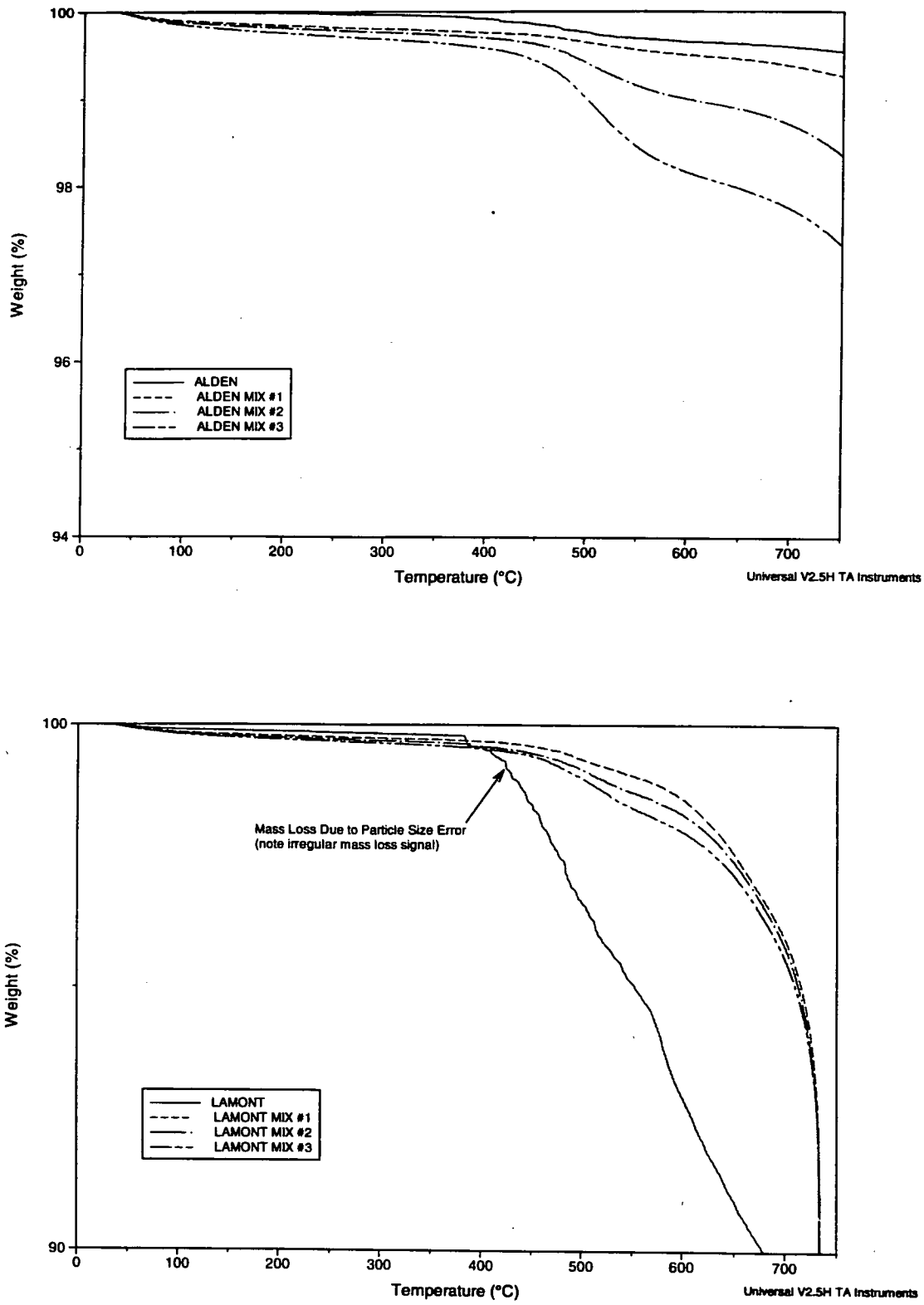


Figure 16. Clay and Dolomite decomposition region for the synthetic standards. Top half of figure illustrates a Calcite (limestone) sample. Bottom half of figure illustrates a Dolomite sample.

Regression results for the Dubberke model.

Service Life = 37 - 3.59*QN

Details:
R= .708, R^2= .5018
F(1,39)=39.290, Std.Error of estimate= 7.90

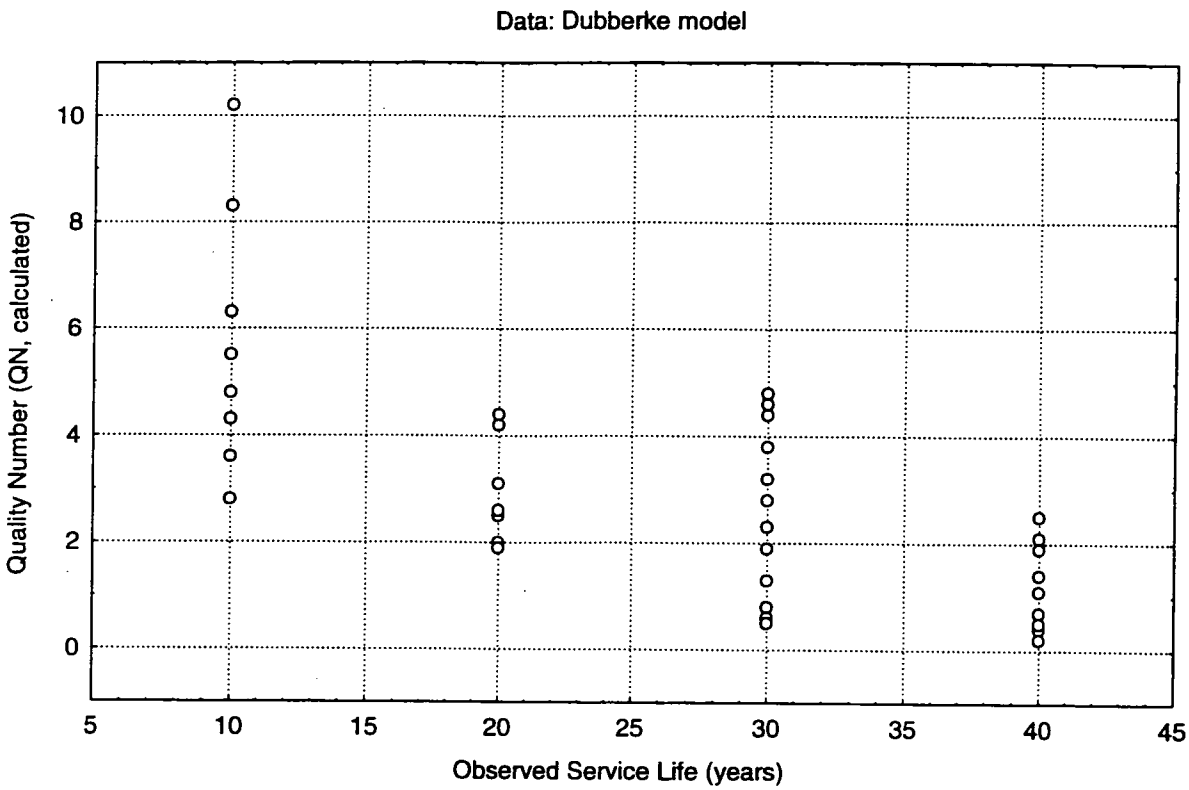


Figure 18. The Dubberke Quality Number model versus observed service life.

clay content influenced the slope of the thermal curve just before the decomposition of calcite. Increasing clay content correlated strongly with the slope of the thermal curve. At the higher clay contents the thermal curves in this region become increasingly nonlinear; and hence, the slope estimates become less reliable because they were based on linear estimates. As was mentioned earlier, the clay decomposition event was most probably completed prior to 800°C and the rapid loss of mass between 850°C and 900°C is most likely due to a breakdown in the carbonate structure rather than the clay structure. However, the exact mechanism of the thermal event is still not entirely clear. The proposed modifications to the carbonate mineral calculation procedure have been summarized in Appendix 4. The modifications have no effect on the quality number calculations because the current quality number calculations only rely on slopes prior to the decomposition events rather than accurate mass loss determinations.

Prediction of Service Life From Chemical and Physical Tests

Dubberke's research clearly indicated that service life exhibited a good correlation to the chemical and physical tests that were scrutinized in this study (see Figure 18, this correlation was based on a subset of data that had been extracted from the larger database utilized in Dubberke's research). The model that Dubberke developed was based on a linear combination of quality numbers that had been obtained from bulk chemistry and mineralogy, thermal analysis tests and pore index testing (see eqn. 1). The weighting coefficients for the quality numbers were assigned using judgement and experience. An attempt was made to bring the predicted values into good agreement with the observed performance of the pavements. At present the model is able to explain about 50% of the variation that is observed in the dataset. This model has been subjected to considerable scrutiny over the past several months and certain aspects of the model would benefit from appropriate modifications. Refinements of the present quality number model plus some alternative models will be presented in a subsequent report.

$$QN = 0.50 * QN_{chem} + 0.25 * QN_{TGA} + 0.25 * QN_{PI} \quad \text{(eqn. 1)}$$

Where: QN_{chem} = chemical quality number
QN_{TGA} = thermal analysis quality number
QN_{PI} = pore index quality number

preparation technique. The impact of the bias on quality number estimates was only significant for dolomite bearing samples. However, the bias was rather significant for dolomite because of the normalization routine that was used to scale the test results.

4. The test results obtained from the TGA tests are typically very reliable. The major sources of error can normally be attributed to particle size problems (sample too coarse) or the presence of clay minerals in the sample. The most serious discrepancies are normally observed when coarse-grained dolomites are analyzed.

RECOMMENDATIONS

This study has indicated that three of the test methods that are currently used to create information for the calculation of quality numbers can be improved by modest refinements. These refinements will take nothing away from the concept of a "quality number" because that particular concept does not need refinement. The existing database contains many pieces of information that exhibit strong correlations to pavement service life. The purpose of the refinements summarized below is simply to strengthen the measurement processes so that the experimental errors do not overwhelm the sometimes subtle details present in the database.

1. Particle size problems were implicated as causing problems in all three of the test methods. More effort should be directed at ensuring that the sample grinding step produces adequate particle size reduction for all samples. This could be as simple as specifying an additional minute of grinding for certain samples. A quick sieving step could also help to separate the fine fraction from the coarse fraction; and hence, avoid excessive grinding of the softer fraction.
2. An internal standard should incorporated in the X-ray diffraction samples. This allows for the correction of peak position errors due to sample displacement and alignment drift. The mixing technique need not be quantitative.

SUMMARY AND CONCLUSIONS

In summary, three of the four primary testing methods that are used to provide raw data for calculating quality numbers have been studied. The test methods that were evaluated included X-ray fluorescence, X-ray diffraction and thermal analysis. The study was conducted to evaluate the reliability of the various test methods. The results of this research effort can be sumarized as follows:

1. The current X-ray fluorescence method (the loose powder method) does an adequate job of quantifying the bulk chemistry of most carbonate rocks found in Iowa. The strength of the method is sample throughput. The accuracy and repeatability of the method are limited due to specimen preparation errors associated with the loose powder technique and the lack of suitable standard reference materials. The method typically produces good estimates of the specific elements currently used for quality number calculations (i.e., Ca, Mg, Sr, Mn S and P). When more accurate estimates of bulk composition are required two additional techniques, the pressed pellet and fused disk techniques, are available for general use.
2. The study indicated that there were only slight discrepancies (typically less than 10% relative error) in the elemental concentrations predicted using the new XRF spectrometer versus those obtained from the old XRF spectrometer. The data in the database was normalized to match the results from the new XRF spectrometer because of its much improved sensitivity to most elements.
3. The X-ray diffraction test results indicate that some biases have probably crept into the database. This study suggested that the major discrepancies were caused by an error related to sample displacement. The error could have been caused by the specimen holders and/or the packing procedure used during sample preparation. Particle size problems probably also played a role. Future measurements can be significantly improved by a slight modification of the current sample

developing models to categorize their concrete aggregates [16, 17]. This may be due to the fact that existing ASTM standards have changed little in recent years. Little effort has been expended to develop new test methods to better categorize aggregates. Instead, we are still left with only a single specification (ASTM C 33) that relies on a wide variety of descriptive test methods or quality test methods that make few attempts to measure fundamental aggregate properties. This is certainly not where Larson et al [2] thought that we would be at the start of a new millenium. Their recommendations for additional research on the physio-chemical properties of aggregates were:

> "The investigation of physio-chemical properties of aggregates and their relation to properties of concrete is a fertile field for future research. It is envisioned that such research would include (a) quantitative evaluation of influence of physio-chemical properties on the performance of aggregate in concrete, and (b) stress model studies using, for example, photoelastic techniques as described in "Miscellaneous Possible Approaches," with materials of known physio-elastic properties to analyze stress distributions versus environmental changes.
>
> From the standpoint of basic research, the work suggested would fill current gaps in the state of knowledge of concrete aggregates. From the applied research view, assembly and correlation of such data could help to provide and index or criterion for aggregate properties as related to their ability to produce durable concrete under specified environmental conditions (see "Miscellaneous Possible Approaches"). However, realization of these broad goals is beyond the scope of the current study."

The goals were outside of their reach in the 1960's; however, that is not the case now. Recent NIST work has used computer modeling to calculate stress fields in concrete. The topic of this report documented a series of fundamental measurement strategies that can be used to estimate pavement service life (limited to Iowa carbonate stones at this time). Perhaps the broad goals summarized above are finally being realized.

The fact that quality numbers are simply correlations to field service life is troubling to this author for two basic reasons. First, the estimation of field service life is a difficult task. It is the absolute slowest way to evaluate concrete performance; and hence, it does not produce immediate feedback

However, for the little additional effort of recording the masses of the internal standard and the sample that were combined, one would obtain quantitative estimates of the minerals present in the samples. Silicon metal (Si, semiconductor grade, passing a 45-micron sieve) has been found to be adequate for routine use. The error correction procedure summarized in Appendix 2 should be used to correct the diffraction data prior to being used for quality number calculations.

3. Corrections should be applied to the existing XRD database to help minimize the influence of the sample positioning errors that were described earlier in this report. The Quartz (101) peak could be used to correct the peak positions observed for Calcite and Dolomite.
4. The relative intensity values stored in the X-ray diffraction database should be converted into semiquantitative concentrations because this would make the information more useful in checking the other two analytical techniques (XRF and TGA). The concept here is to construct redundancy in the various measurements so that cross checks can be conducted routinely. This will help to strengthen the overall integrity of the database.

CLOSING COMMENTS

The strength of the quality number concept originates from the fact that aggregates can now be evaluated quickly (hours or at most a day or two) rather than the days, weeks or months that used to be required. This allows much more flexibility in using the technique for the quality control and quality assurance aspects of aggregate production. However, it is important to realize that the quality number method is still just a correlation of several diagnostic tests to field service performance. The method is also new and will undergo considerable refinement before it reaches maturity. It is also important to realize that researchers in other states are very interested in

when the multitude of other materials that are commonly used in modern concrete could be changing significantly. By the same reasoning, innovations in construction practices have the potential to cloud the estimation of service life because innovation often has its early failures while the new (unforseen?) problems that they cause are being worked out. And secondly, it presents only a stochastic view of aggregate quality. It makes no effort to determine why some aggregates remain durable for 40 years (or more!) while others exhibit cracking in only about 10 to 15 years, we simply accept the observed behavior. Ideally, this author thinks that one would be more confident with a model that takes into account the underlying reason (i.e., mechanism) that causes an aggregate to fail. A mechanistic model would also allow more flexibility when materials properties or construction practices change. However, such a model would require fundamental research on some topics that have troubled concrete researchers for the past 50 years. Dolch [18] has clearly stated why he thinks that the current trend toward "practical" research has circumvented our real need in the area of concrete science, the need to grasp an understanding of the fundamental processes that occur in portland cement concrete systems.

ACKNOWLEDGEMENTS

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Appendix 1 (Standard Operating Procedures for XRF)

XRF Standard Operating Procedures

Summary

1.0 Sample pretreatment is an important step in the analysis process. Most carbonate stone assays are reported on a dry basis so the basic premise is that the samples have been dried to a constant mass.

1.1 Samples are dried at a temperature of about 115 to 120°C. The duration of the drying period varies depending on the particle size of the sample. Small aliquots (gram portions) of fine powders typically dry in about 2 hours. Overnight drying is recommended for kilogram portions of bulk rock samples. The "Free Moisture" procedure described in ASTM C 25 [8] summarizes the basic steps and appropriate calculations needed to define the moisture content of a limestone sample.

1.2 Samples are ground to a fine particle size using a SPEX shatterbox and hardened steel or corundum grinding vessels. Grinding time typically varies from 2 to 10 minutes for carbonate rocks. Grinding time normally increases as the silica (quartz) content of the rock increases. Grinding times in excess of 15 minutes are normally not used because they can contaminate the sample with small amounts of iron and manganese. Also, extended grinding can damage the crystal structure of carbonate minerals. This can be avoided by using a wet grinding technique using alcohol or propylene glycol; however, this requires an additional drying step in the sample preparation procedure.

1.3 Carbonate rocks exhibit large mass losses when they are heated above 900°C. This mass loss is predominately due to the liberation of carbon dioxide from the rock as it decomposes; however, clay minerals can also contribute to the mass loss that is observed. . The "Loss on Ignition" procedure described in ASTM C 25 [8] summarizes the basic steps and appropriate calculations needed to define the loss on ignition of a limestone sample.

2.0 The loose powder technique is the simplest and quickest method that can be used to prepare samples for XRF analysis.

Equipment Required:

Disposable sample cups with closure rings

PROLENE film (4 microns thick)

Balance or scale

Standard Operating Procedure:

2.1 Arrange the samples into a sample queue that meets the needs of the analyst. It is assumed that the samples have been ground as defined in section 1.2 above.

2.2 Set a disposable sample cup on top of each of the samples arranged in section 2.1.

2.3 Use a magic marker to label the top of the disposable sample cup with the name of the sample that it is sitting on. Repeat this process until all of the samples have a matching disposable sample cup with the proper sample name marked on it.

2.4 Using the balance (scale) on the bench place a mass of 2.5 to 3.0 grams into the appropriate sample cup. Repeat this process until all of the samples have been prepared.

2.5 Seal each sample cup with the PROLENE (4.0 microns) X-ray film and a retainer ring. Take care to make sure that film is snug and taut in the sample cup. Wrinkles will distort the measurement of light elements in the samples. Repeat this process until all of the samples have been processed.

2.6 Tap the sample cup (face down) about five (5) times on a clean surface to gently pack the loose powder into the cup. Repeat this process until all of the samples have been processed.

2.7 Look at the back of each sample cup to make sure that the plastic tab is open. This is done to ensure that the helium purge gas can enter the sample cup to equalize the pressure on both sides of the PROLENE film.

2.8 The samples are now ready for XRF analysis – refer to section 5.0 below.

3.0 The pressed pellet technique uses a fixed amount of sample, a binder and a sample press to construct a "pellet" of each sample. The pellets are very durable and do not suffer from the packing problems or film problems that can cause difficulties for the loose powder method. In addition, the pressed pellets can be analyzed in a vacuum so that they produce the best analyte response curves for the XRF methods used in this study. Hence, they are useful when measuring minor or trace elements in any given sample.

Equipment Required:

X-ray mix powder

Boric acid tablets (0.5 gram per tablet)

Balance or scale

SPEX pellet press

SPECAP pellet die with two hardened steel platens and a plunger

Aluminum sample cups (40 mm diameter)

Flaring tool to expand the rim of the sample cups

Vacuum pump

Standard Operating Procedure:

3.1 Samples will be processed in sets of three (3) since this is the number of grinding vessels available on the shatter box.

3.2 Weigh out 8.000 grams of ground up sample, 1.500 grams of X-ray Mix Powder, and 1.0 grams of boric acid (this is equivalent to two (2) boric acid tablets) into a shatter box grinding vessel. Repeat this process for the other two samples in the set of three.

3.3 Grind the mixtures for two minutes in the shatter box.

3.4 Attach the SPECAP die to the vacuum hose

3.5 Place the lower load platen in the die. Make sure that the polished side of the platen is facing up.

3.6 Flare an aluminum sample cup by placing it on the desktop and then pressing the flaring tool into the cup until it stops.

3.7 Place the sample cup into the SPECAP die and push it down until it reaches the bottom load platen.

3.8 Pour the sample mixture into the sample cup. Make sure that the powder is spread out evenly in the sample cup.

3.9 Place the upper load platen in the SPECAP die. Make sure that the polished side of the platen is facing down.

3.10 Place the plunger on top of the upper load platen.

3.11 Turn on the vacuum pump. This should pull the upper load platen and the plunger down into the SPECAP die.

3.12 Place the SPECAP die into the SPEX pellet press and tighten the top screw until it is snug against the top of the plunger.

3.13 Close the needle valve on the right side of the SPEX press.

3.14 Close the front sliding door. Make sure that the microswitch is activated when the door is closed.

3.15 Press and hold the silver button on the front of the press. Hold the button until the SPEX press indicates 26 tons of load has been applied to the sample, then release the button.

3.16 Wait thirty seconds (30 sec.) and then bleed off the load using the needle valve on the right side of the SPEX press.

3.17 Turn off the vacuum pump and allow the vacuum to bleed off.

3.18 Open the front sliding door and remove the SPECAP die from the SPEX press. The top screw may need to loosened before the die can be removed from the press.

3.19 Remove the pressed pellet from the die. It is simplest to turn the SPECAP die upside down (make sure that the plunger is held in place) and then placing it on the table top. Then remove the bottom of the die and push down firmly to eject the pellet. Make sure that the pellet is labeled. Repeat the process with the remaining samples.

3.20 The sample is now ready for XRF analysis – refer to section 5.0 below.

4.0 The fused disk technique is the most robust sample preparation method for XRF analysis. Following is the procedure for preparing specimens. The samples will be melted, or fused, into glass disks and this makes it necessary to know the loss on ignition of each sample so that the appropriate dilution factor can be maintained. The loss on ignition test should be conducted as outlined in section 1.3 or an equivalent LOI-free amount of sample should be weighed out using the following equation. This method uses a flux to sample ratio of 5.00.

LOI-free mass (grams) = 1.200/(1 - %LOI/100)

4.1 Flux Preparation

4.1.1. IMPORTANT NOTE – clean and dry the ceramic bowl prior to placing the flux in it. Flux can be contaminated with small amounts of common elements if proper analytical precautions are not observed.
4.1.2. Ignite 100 g of flux in a ceramic bowl for 3 hours at 450±25°C.
4.1.3. Do not overheat the flux, monitor the temperature regularly during the three hours.
4.1.4. Cool the flux for 2.0 hours in the desiccator.
4.1.5. Reweigh the flux to calculate loss on ignition and record value in appropriate file.

4.2 Sample Preparation. This procedure outlines the weighing of the mixture of flux and bulk sample. The bulk samples needed were prepared using the guidelines set forth in section 1. ***The following procedure should only be performed by properly trained personnel since lithium tetraborate is a hazardous chemical.***

4.2.1. Take out of the 105 degree oven X glass vials along with the two glass weighing boats and put them in a desiccator to cool for approximately 30 minutes.
4.2.2. After cooling, use the large weighing boat to weigh out 6.000±0.001 grams of Lithium Tetraborate (LECO TYPE F flux). Pour the flux from the weighing boat into a glass vial.
4.2.3. Recheck the mass of the weighing boat to ensure the proper amount of flux was transferred to the vial, keeping the above range in mind.
4.2.4 Using the small weighing boat and a different spatula, weigh out 1.200±0.0005 grams of sample. Pour the sample from the weighing boat into the vial with the flux.
4.2.5. Using the spatula, stir the sample and flux together in the vial to create a homogeneous blend.
4.2.6. Label the vial accordingly.
4.2.7. Wipe both spatulas and both weighing boats clean before proceeding to the next sample.
4.2.8. Repeat steps 4.2.2 through 4.2.7 for all samples.
9. After finishing with the weighing boats, wash them with distilled water, and wipe dry with a kimwipe. Place them back in the 105 degree oven.

4.3 Fusing the flux-sample mixture into a glass disk. This procedure details the steps that are required to produce good glass disks. The safety notes should be reviewed before proceeding. The following procedure should only be performed by properly trained personnel.

Safety Notes: (These apply to people using the LECO FX-503 Fluxer)

Use the fume hood! This is a high temperature procedure, and the fume hood will pull some of the heat away from the surrounding area. It also ensures that the operator is not exposed to any toxic vapors.

Once in operation, the fluxer and anything that comes out of it is extremely hot. Use caution in handling crucibles and casting dishes, and wear the protective gloves whenever possible.

The flux used has a high melting point, so a vigorous flame is used. Stand away from the fluxer during operation and wear all appropriate safety items when operating the machine. NEVER leave the machine unattended - you should always be in the same room when the burners are activated and running.

Equipment Required:

3-Platinum/gold crucibles	3-Platinum/gold casting dishes
1-Platinum or Nichrome tongs	1-Pair of heat-resistant gloves
1-Flask of LiBr soln.	1-Disposable pipette/bulb
labels for fused samples	1-Container for sample storage
1-Ceramic plate (to set hot items on)	

Note 1: The process time for each set of samples is approximately 20 minutes. You will be working with three samples simultaneously, so organization will be important to keep samples from being improperly labeled.

Note 2: At any time during the following procedure, the fluxer can be stopped and shut off by pressing the EXIT key. Keep in mind all safety precautions listed at the beginning of this section.

4.3.1. Take out all supplies listed above from the storage cabinet under the fluxer.
4.3.2. The fluxer should have the power on, and the display screen should be on the main menu.
4.3.3. Wipe clean the top of the fluxer with a damp paper towel to keep samples from being exposed to any contaminants.
4.3.4. Open the slide on the fume hood vent above the fluxer and turn on the fume hood fan.
4.3.5. If necessary, open the air valve to the left of the fluxer, making sure it is completely open (turn until it stops).
4.3.6. Open the primary and secondary valves on the propane tank located in the storage cabinet under the fluxer, making sure both are completely open (turn both until they stop).
4.3.7. Get the samples ready for fusion. Set the crucibles on a paper towel on a lab bench. Take one of the glass vials with the sample and flux already mixed together, put the crucible over the top of the vial, and invert both to empty the sample into the crucible. Slowly remove the vial. Tap the outside of the vial to release any residue and add this to the crucible. **Important:** Inspect the vial to make sure as much of the sample as possible has been transferred to the crucible. Repeat this process for the other two samples.
4.3.8. Using the disposable pipette and bulb, add two drops of the LiBr solution to each crucible. It is not necessary to mix this into the sample. The crucibles are now ready.

Instructions for making the LiBr solution are summarized below (see Note 3).
4.3.9. From the methods selection list, SELECT the method entitled "CARB. ROCK" by using the NEXT or PREVIOUS keys to toggle through the different methods. Then press the SELECT key.
4.3.10. The next display asks for which burners to use. Press the 1,2, and 3 keys (assuming that you want to process three samples, you can use each burner individually if there are not enough samples to form sets of three for each run).
4.3.11. Press the START key to initiate the fluxer cycle.
4.3.12. A notice will appear to have all crucibles and casting dishes loaded. Open the door to the fluxer and carefully load each crucible into the metal holders. Insert the rim of each crucible so they sit in the groove and slot of each holder. They should be able to move only a few millimeters back and forth when in place. Then carefully load the casting dishes into their holders. Quickly check to ensure they are relatively level and the ceramic holders are seated properly.

Note 2: At any time during the following procedure, the fluxer can be stopped and shut off by pressing the EXIT key. Keep in mind all safety precautions listed at the beginning of this section.

4.3.13. Close the door to the fluxer.
4.3.14. Press START again to ignite the burners and start the cycle timer. **Stand back while the burners are igniting!**
4.3.15. At the end of the cycle, the crucibles will tip forward for easy removal. Everything is extremely hot after the run, so wear the yellow safety gloves to unload both the crucibles and the casting dishes. The crucibles can be unloaded by simply spreading the holders apart and removing the crucibles with a gloved hand. The casting dishes should be removed with the tongs, set on the open door, and then can be handled by gloved hands.
4.3.16. Leave the door open and the fluxer as is. This will make it easy to reload the casting dishes for the next run.
4.3.17. Allow the crucibles to cool for approx. 2 minutes before handling without gloves. The samples will be cool after about 3-5 minutes.
4.3.18. Clean any residue out of the crucibles, wipe them clean (see Note 4).
4.3.19. After the samples have cooled (approximately 5 minutes), apply labels to the top surface, the side being analyzed is the side in contact with the bottom of the casting dish. Do NOT touch the analytical surface of the specimens.
4.3.20. Repeat steps 4.3.7 through 4.3.19 until all the samples have been fused into glass disks.
4.3.21. The specimens (glass disks) can now be placed in the spectrometer for analysis or they can be stored in a container until all of the samples have been fused.
4.3.22. When finished with all samples, press Exit twice to return the fluxer to its neutral position and to the main menu.
4.3.23. Shut off both gas valves on the propane tank (turn both valves to the right until they stop, just snug – there is no need to overtighten the valves).
4.3.24. Close the slide on the fume hood vent above the fluxer.
4.3.25. Shut off the fume hood fan.
4.3.26. Dispose of the pipette in the broken glass container in room 62.
4.3.27. Return all supplies to the cabinet below the fluxer.
4.3.28. Clean the crucibles if necessary.

Note 3: LiBr Solution Preparation **The addition of water to the LiBr is very exothermic, caution should be exercised in making the solution.**
1. Weigh out 25 grams of LiBr and put it into a 100 mL volumetric flask. Use a flask that is easily stoppered or corked.
2. Add cold water to the mark on the flask.
3. Mix the solution well and allow to cool before using.

Note 4: The crucibles should be clean before starting the following procedure - the smallest amount of contaminant can effect the end result. The crucibles should always be cleaned before making standards, and they should be periodically cleaned during regular usage. The crucibles can be gently boiled in dilute HCl acid for a few minutes to remove any residue. ONLY USE DILUTE HCl, never use a blend of acids. A solution of approx. 9% HCl is available in the storage cabinet under the fume hood. Also, remember that the crucibles are to be handled with care. Scratches, dents, or dings in the crucibles make them less efficient; the flux will not flow as easily out of them. Never use anything harder than a fingernail to remove any residue in the crucibles after a run in the fluxer.

5.0 Operating the PHILIPS PW 2404 X-ray Spectrometer (XRF). It is assumed that the operator is familiar with operating personal computers that utilize the Windows 95 operating system. For the purpose of this documentation, input requests, such as the selection of menu or drop down box items, have been surrounded by quotation marks (i.e., "File"). Other input requests, such as push buttons, view tabs or other icons, have been placed in brackets (i.e., [OK]). The quotation marks and brackets will not appear on the computer screen.

5.1 The computer used to control the XRF is normally left on and Windows 95 is already loaded. Always move the mouse or press a key on the key board to deactivate the screen saver before you attempt to restart the computer. If the computer has been turned off then simply press the POWER button on the computer. This automatically loads Windows 95.

5.2 The SUPERQ measure and analyze program is normally left running. If the program is running then skip to step 5.5 below. If the program has been terminated then select the START icon in the lower left side of Windows task bar followed by the RUN XRF icon. This will start the SuperQ Manager. Depress the [Measure and Analyze] button on the SuperQ Manager. Note, that the SuperQ manager can also be started by double clicking on the "RUN XRF" icon on the Windows 95 desktop.

5.3 SuperQ will check the integrity of the sample results database and then it will request a User Name and a Password. Valid user names for the Iowa DOT are: Chem and Materials
Passwords will be assigned by the system manager.

5.4 SuperQ will now send the appropriate database configuration parameters to the spectrometer. This process may take several minutes (note the yellow status bar at the bottom of the child window), the system will be

inactive until this process is completed. If the process returns an error message or a message box please inform the appropriate MARL staff before proceeding.

5.5 Prior to running samples it is best to warm up the spectrometer. This is done by:
a.) Press the green [OPEN] button on the spectrometer
b.) Wait for the light in the [OPEN] button to illuminate
c.) Open the lexan cover to the sample changer
d.) Place the STEEL sample in the sample entry port
e.) Go to the XRF computer
f.) Choose menu selection "Measure sample"
g.) Select "WARMUP" from the application box
h.) Press [MEASURE]
i.) When the application is finished press [OK]
j.) Walk to the spectrometer and remove the sample
k.) Put the sample back in position Y1 for future use

5.6 Open a sample list by choosing the menu selection "Measure" followed by "Open a sample list". Choose the sample list denoted as "Carbonate Rocks" and depress [OK]. This will bring up the Sample list – CARBONATE ROCKS child window. This child window allows several ways to view the samples on the sample changer, the views are controlled by the tabs near the top of the window. The first tab [Sample changer map] shows a diagram of the positions available on the automated sample changer. The second tab [Measurement sample queue] simply lists the samples in the order that they will be analyzed. Users need not be concerned with the remaining two tabs at this time.

5.7 Since the Carbonate Rocks application is routinely used by IA DOT personnel there may be many samples in the sample queue at any given time. Hence, the first step is to check to see if the sample has been analyzed. A green check mark next to the sample ID indicates that the sample has been analyzed. After samples have been analyzed, they can be removed from the sample queue by:
Select the [Measurement sample queue] tab. Click the mouse cursor in the "No" column on the top left side of the form. This will highlight (in green) all of the samples in the sample queue. Deselect the samples denoted as "AUS011" and "CARBONATE RUN MONITOR" plus any samples that do not have green check marks by clicking on the sample number. This will cause the selection to change to a gray color. To remove the selected (green highlighted) samples press [REMOVE] and then [OK].

5.8 Place the samples that you want to measure in the steel sample cups that have been numbered from 1 to 40. There are a variety of different cups available but only the numbered cups can be used for the Carbonate Rocks application. Typically, the sample positions on the left side of the sample changer are used as measurement positions. These locations

are designated as A1 through A12, C1 through C12 and E1 through E12 from front to back.
Make sure that the samples fit precisely in the sample cups, the sample surface should sit directly against the steel bottom of the cup. This can be checked by picking up the cup and inspecting the analytical surface of the sample. Also, severe wrinkles in the PROLENE X-ray support film should be avoided.

5.9 Note the location of the samples on the sample changer. The AUS011 and CARBONATE RUN MONITOR must be placed in the positions designated on the sample queue.

5.10 Lower the lexan cover to the spectrometer. The light on the green [OPEN] button will go out when the cover is closed.

5.11 Go to the XRF computer and enter the sample names into the sample queue. This is done by:
Pressing the [+ SAMPLE] button
Setting the "Archive" to "Carbonate Rocks"
Setting the "Application" to "Carbonate Rocks"
Entering the sample name
Selecting the position of the sample on the sample changer
Pressing the [+ NEXT] button

After the [+ NEXT] button has been pressed you will note that the sample position has been incremented to the next position and the "Archive" and "Application" selections are already set to "Carbonate Rocks." Hence, subsequent samples for the same application can be entered by:

Entering the sample name
Entering the sample location
Pressing the [+ NEXT] button

When all the samples and sample changer positions have been entered press [OK] to terminate the data entry step.

5.12 Recheck the sample queue to make sure that the sample positions listed on the computer exactly match the location of the samples on the sample changer.

5.13 Press [START] on the upper right hand side of the sample queue form. This will start the sample changer and it will automatically process the samples. More samples can be added to the sample queue when cups become available (i.e., after the samples have been analyzed). Refer to steps 5.7 through 5.12 listed above. Always remember to press the green [OPEN] button and waiting for the light in the button to illuminate prior to opening the lexan cover. Also, the cover must be closed (make sure the light on the button is off) before the automatic sample changer will pick up samples.

5.14 When all the samples have been analyzed press [OK]. If you are finished measuring samples then press the [End of List] button. Then remove your samples from the sample changer.

5.15 To shut down the spectrometer do the following:
a.) Press the green [OPEN] button on the spectrometer
b.) Wait for the light in the [OPEN] button to illuminate
c.) Open the lexan cover to the sample changer
d.) Place the STEEL sample in the sample entry port
e.) Go to the XRF computer
f.) Choose menu selection "Measure sample"
g.) Select "SHUTDOWN" from the application box
h.) Press [MEASURE]
i.) When the application is finished press [OK]
j.) Walk to the spectrometer and remove the sample
k.) Put the sample back in position Y1 for future use

Note, that by placing the STEEL sample after the last sample in your sample queue and then entering the appropriate archive (SHUTDOWN), application (SHUTDOWN) and sample position (Y1), you can have the spectrometer shut down automatically.

Appendix 2 (Standard Operating Procedure for XRD)

XRD Standard Operating Procedures

Summary

1.0 General precautions. Only properly trained personnel should use the X-ray diffractometer (XRD). X-ray diffraction analysis makes use of high voltage equipment that produces a very intense X-ray beam. The X-rays used in typical diffraction experiments can cause serious burns on the hands and fingers if appropriate safety precautions are not observed. The SIEMENS D 500 diffractometer available in this lab is equipped with a safety circuit that greatly minimizes the likelihood of getting an X-ray exposure. **NEVER** defeat the X-ray safety circuit for any reasons. Only professional X-ray technicians can operate the diffractometer when the safety circuit has been shorted. IMMEDIATELY contact a MARL employee to report any abnormalities in the function of the diffractometer.

2.0 Specimen preparation – side loading. Current Iowa DOT test specimens for X-ray diffraction are prepared by side loading. This technique produces a good, reproducible sample surface that exhibits only a minimal amount of preferred orientation. The basic steps can be summarized as follows:

2.1 Take the XRD specimen holder and place the plexiglass cover over its top surface. The specimen holder and the plexiglass cover must remain securely mated together during the process of placing the sample into the holder. This ensures that the top surface of the sample will remain coincident with the top of the specimen holder – this is a necessary constraint in any diffraction experiment.
HINT: A large binder clip can be used to securely fasten the specimen holder to the plexiglass cover. This clip can be removed when the sample loading is completed.

2.2 Position the sample entry hole up so that the powdered sample can be poured into the specimen holder.

2.3 Pour the powdered sample into the specimen holder. Use a thin spatula to aid the filling process. Continue filling the specimen holder until it is slightly overfull. Then gently tap the specimen holder on the table to compact the powder in the holder. Add additional powder and repeat the tapping process until the specimen holder is totally filled.

2.4 Carefully place the specimen holder and plexiglass cover on the tabletop. Lift off the plexiglass cover (do not slide off the cover because this can orient some of the crystals in the holder). Check the surface of the sample to make sure that it is just even to the top surface of the specimen holder.

2.5 The specimen is now ready to be placed in the diffractometer. Refer to section 3.0.

3.0 Collecting a diffractogram. The SIEMENS D 500 diffractometer is controlled by a computer. The computer automates the data collection and data reduction steps of the analysis. The computer cannot insert the specimen into the diffractometer, energize the X-ray tube or open the shutter of the X-ray tube. These steps must be performed manually. Data for carbonate rocks should be stored on the computer hard drive in the C:\DOTXRD\ROCKS subdirectory. This greatly simplifies finding the appropriate files for future reference. The computer automatically saves the data files during the data acquisition process. It is assumed that the operator is familiar with the Windows 95 operating system and that the XRD Computer is already running. If the computer has been shut off then simply press the [ON] toggle to start the computer. The computer will automatically load the Windows 95 operating system. Always move the mouse or press a key on the key board to deactivate the screen saver before you attempt to restart the computer.

3.1 Go to the XRD computer and double click on the RUN XRD FOR IADOT icon on the Windows 95 desktop. This starts the DATASCAN program.

3.2 Go to the X-ray generator and set the high voltage to 50kV and the filament current to 25mA. This is done by:

Pressing the [kV] button on the generator
Entering [5] and [0] on the key pad
Pressing [ENTER] on the key pad

Pressing the [mA] button on the generator
Entering [2] and [5] on the key pad
Pressing [ENTER] on the key pad

3.3 Press [13] on the Manual Control Panel. This shuts off the X-ray beam so that the glass door to the diffractometer can be opened.

3.4 Open the glass door to the X-ray diffractometer and remove the gold specimen carrier from the center of the diffractometer.

3.5 Check the divergence slits (denoted as I, II and III) to make sure that they are set at 1°. Also, check the detector slit (denoted as IV) to make sure it is set at 0.05°. These are the normal settings used for X-ray diffraction experiments by the Iowa DOT.

3.6 Place the specimen holder containing the sample into the specimen carrier.

3.7 Place the specimen carrier into the X-ray diffractometer. The diffractometer has a magnetic seating mechanism and you should feel the specimen carrier snap firmly into place.

3.8 Close the door to the diffractometer.

3.9 Turn on the sample spinner. This is done by turning the control toggle to [I] on the Manual Control Panel.

3.10 Press [14] on the Manual Control Panel to open the X-ray shutter.

3.11 Return to the XRD computer – the DATASCAN program should still be running.

3.12 Press the [SCAN] button at the top left side of the form.

3.13 Press the [Files: C:\ .....] button at the top middle of the form. This button sets the subdirectory that will be used to store the data it should be set to C:\DOTXRD\ROCKS for normal data collection procedures. Note the file name of the last file that was written to the subdirectory. These are normally entered at MEASXXXX.MDI, where the XXXX indicate integer file numbers between 0000 and 9999.

3.14 Enter the appropriate file name in the [Auto-file ID] input box. NOTE: you can also press the up arrow on the combo box to increment the file name in integer units.

3.15 Choose the [Carbonate Rocks] scan from the drop down box to the right of the [Set-up] button.

3.16 Type the sample name into the Scan ID input box.

3.17 Press [START] at the lower right side of the form.

3.18 The computer will now ask you if you are ready to proceed. Respond [YES] and the computer will initiate the data collection procedure. The diffractogram will be displayed on the computer screen as it is acquired and the data will be written to the hard drive at 100 point intervals. When the data has been collected the computer will park the diffractometer at 20° two-theta. The data collection procedure can be stopped at any time by pressing the [STOP] bar at the top of the form.

3.19 After the diffraction run is finished press [13] to close the X-ray shutter. This can be done while the computer is parking the diffractometer at 20° two-theta.

3.20 Remove the specimen carrier from the diffractometer and take out the test specimen.

3.21 Repeat steps 3.6 through 3.20 until all of the specimens have been tested.

3.22 When finished collecting all the data go to the X-ray generator and set the filament current to 05mA and the high voltage to 20kV. This is done by:

MAKE SURE YOU LOWER mA before adjusting the kV!

Pressing the [mA] button on the generator
Entering [0] and [5] on the key pad
Pressing [ENTER] on the key pad

Pressing the [kV] button on the generator
Entering [2] and [0] on the key pad
Pressing [ENTER] on the key pad

4.0 Data reduction. Data is analyzed using the JADE 5.0 program. To start this program simply double click on the JADE 5.0 icon on the Windows 95 desktop. The output from the program consists of a plot that lists the location and intensity of the various diffraction peaks that were found in the raw data.

4.1 Use the mouse to select the menu item [File/Patterns].

4.2 Select the subdirectory [C:\DOTXRD\ROCKS]

4.3 Select the file name or file ID that you want to load. This will load the raw data into the computer memory and it will also display a graph of the raw data.

4.4 Press [F2] on the keyboard. This brings up the peak search form.

4.5 Choose the appropriate output details, these details are chosen from the checkboxes on the [Labeling] tab. Once the check boxes have been selected, they should stay that way until the program is terminated. The normal output includes the line marker, d-spacing and intensity. Vertical labels work the best.

4.6 Press the [Apply] button at the bottom, right side of the form. This calculates and displays the items that were selected. Check to make sure that the peak positions agree with the line markers.

4.7 Press the [Close] button when you are satisfied with the results of the peak search.

4.8 Press the printer icon on the top tool bar to print the results. The results will come out on the laser printer unless a different printer is specified. Color output can be obtained by directing the results to the EPSON 600 printer.

4.9 Repeat steps 4.1 through 4.8 until all the files have been processed.

5.0 Data correction procedures. Data from an X-ray diffraction experiment is subject to several sources of error. The major source of error normally comes from sample positioning errors. This can be due to poor specimen loading techniques, poor sample preparation or a defective specimen holder. The following examples will provide a standard correction procedure that can be used to minimize the influence of sample positioning errors. These correction procedures can be invoked interactively in the JADE software. The correction procedures can be used to create correction curves for individual sample holders. However, the most exact measurements always include an internal standard.

Example 1: Correcting data via an internal standard using a single peak.

An X-ray diffraction pattern was collected using the standard IaDOT setup and measurement parameters. The sample had been mixed with 10% Si metal prior to the analysis. This was done by weighing out 2.70 grams of sample and 0.30 grams of Si metal and then mixing them together using an agate mortar and pestle. A tabulation of the correction procedure is as shown below.

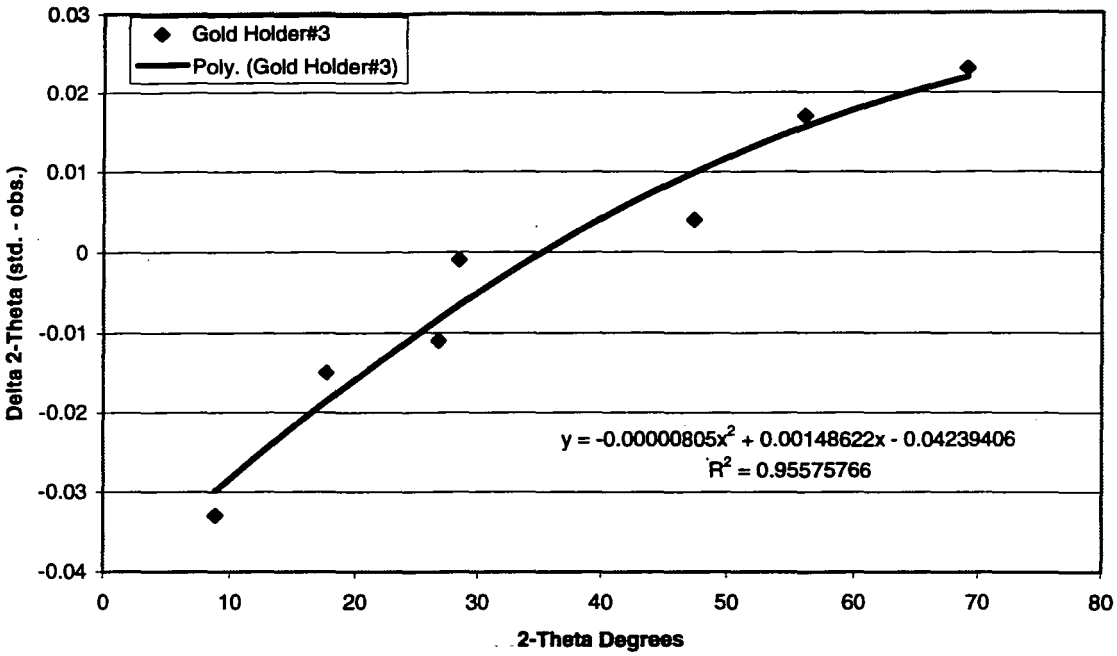
Measured XRD peaks (2-theta, °)	Std. Peaks Si, Theory (2-theta, °)	Correction (theory - obs.) (2-theta, °)	Corrected Peaks (2-theta, °)	Comparison to Theory (2-theta, °)
26.622			26.641	26.651
28.423	28.442	0.019	28.442	28.442
29.400			29.419	29.405
30.939			30.958	30.960

Example 2: Correcting data via an internal standard using a series of peaks.

This is just an extension of example 1. Multiple reflections of a standard are measured and a smooth curve is fit to the data (see the figure on next page). The data is normally fit with a first or second order polynomial. After correction, the peaks generally agree within about ±0.005° 2-theta of the theoretical peak locations. This is a substantial improvement in accuracy over the peak positions that were determined from the raw data.

Measured XRD peaks (2-theta, °)	Standard Peaks Theory (2-theta, °)	Difference (theory - observed) (2-theta, °)	Corrected Peaks (2-theta, °)
8.886	8.853	-0.033	8.856
17.774	17.759	-0.015	17.755
26.785	26.774	-0.011	26.777
28.443	28.442	-0.001	28.436
47.299	47.303	0.004	47.309
56.105	56.122	0.017	56.121
69.107	69.130	0.023	69.129

Figure illustrating the correction curve discussed in Example 2.



Appendix 3 (XRF Verification Memo)

May 6, 1998

To: C. Narotam
J. Lane
B. Gossman
B. Dawson
P. Hockett
V. Marks

From: T. Hanson

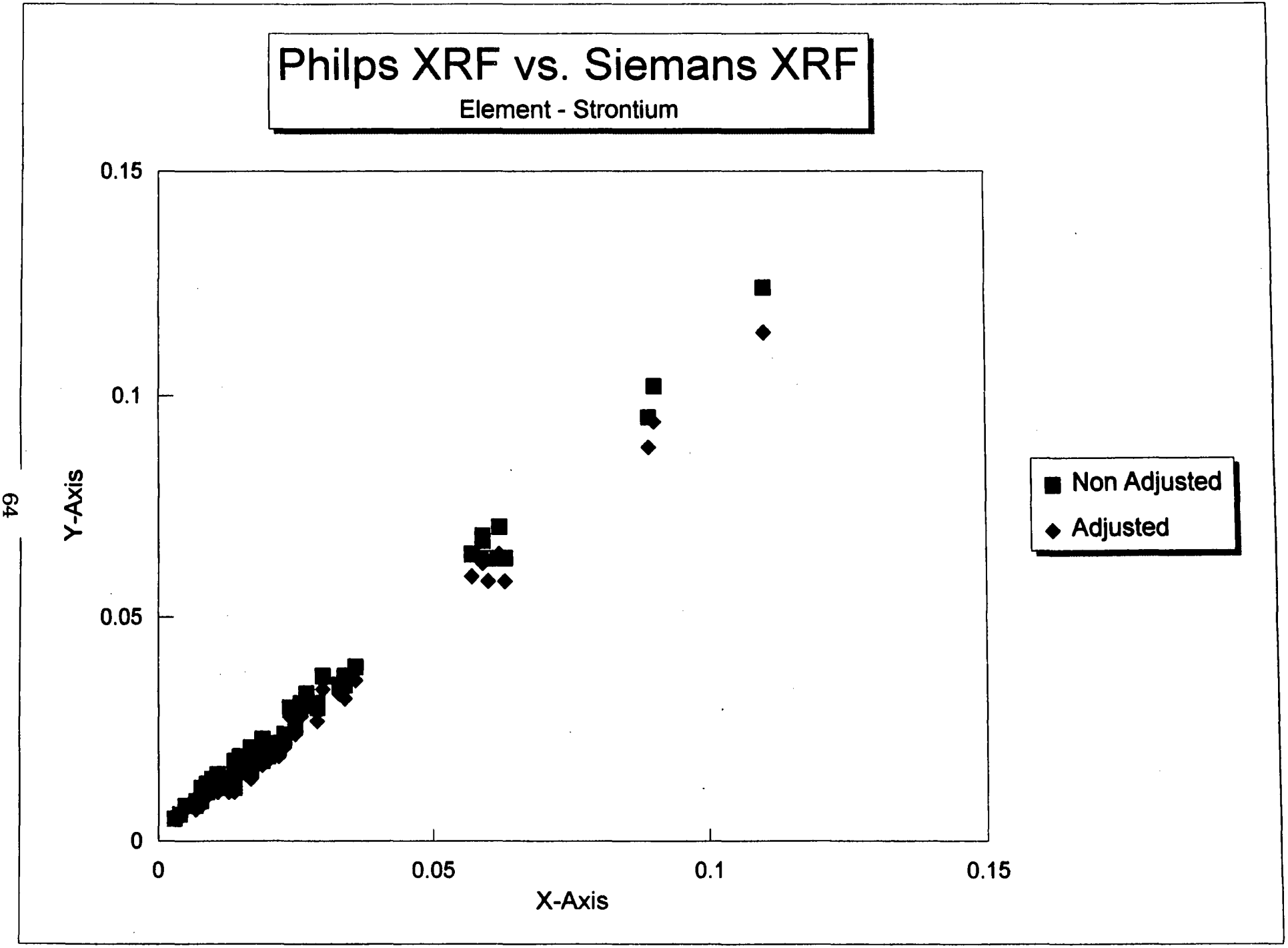
Subject: Carbonate Aggregate Element Analysis - Siemans XRF vs. Philips XRF

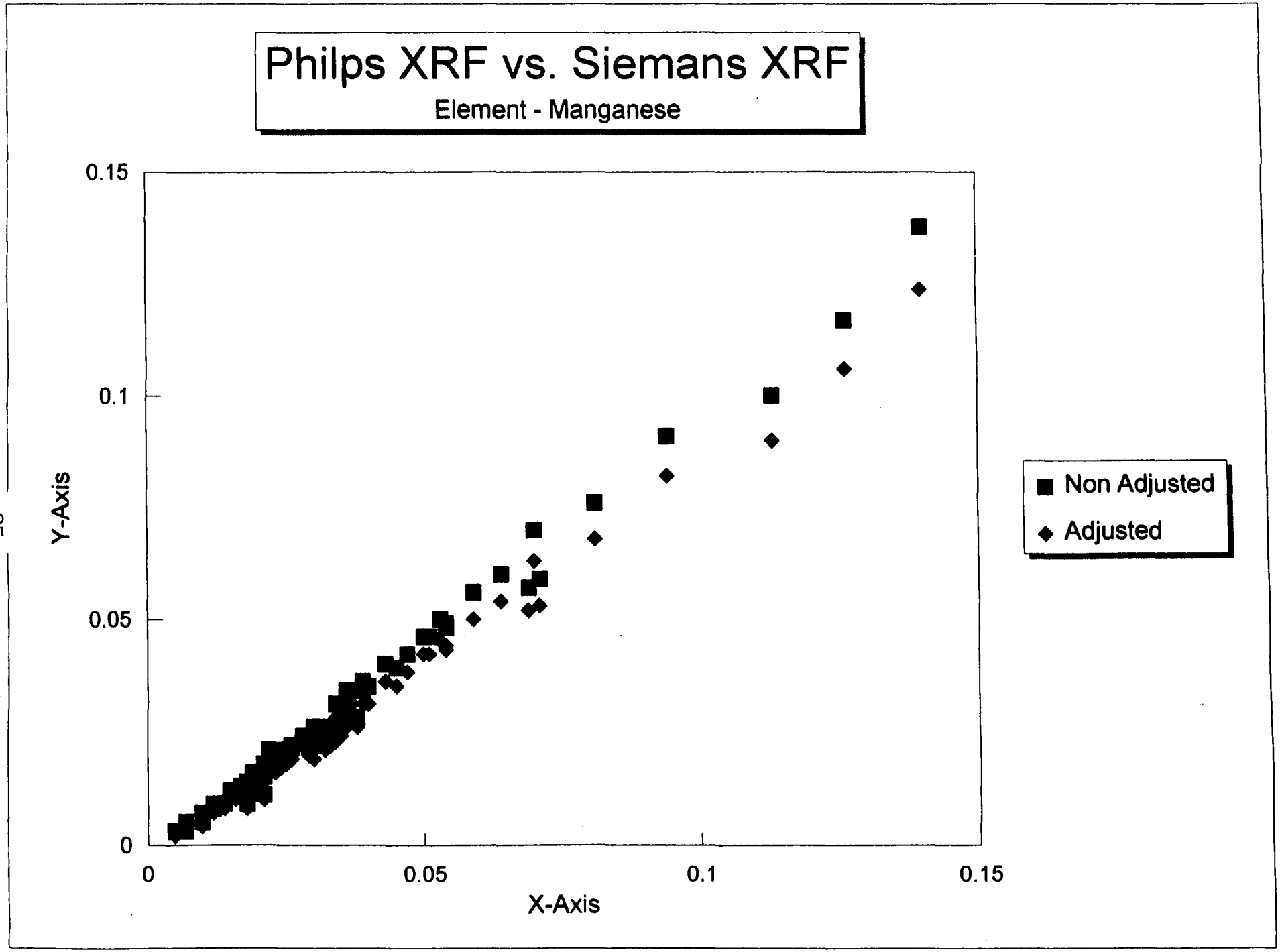
Scott Schlorholtz and Wendell Dubberke completed validating the new Philips XRF matches the data obtained from the Siemans XRF of which over 7000 samples have been analyzed. Scott has reran approximately 100 samples using the new Philips XRF which have been previously ran on the Siemans XRF.

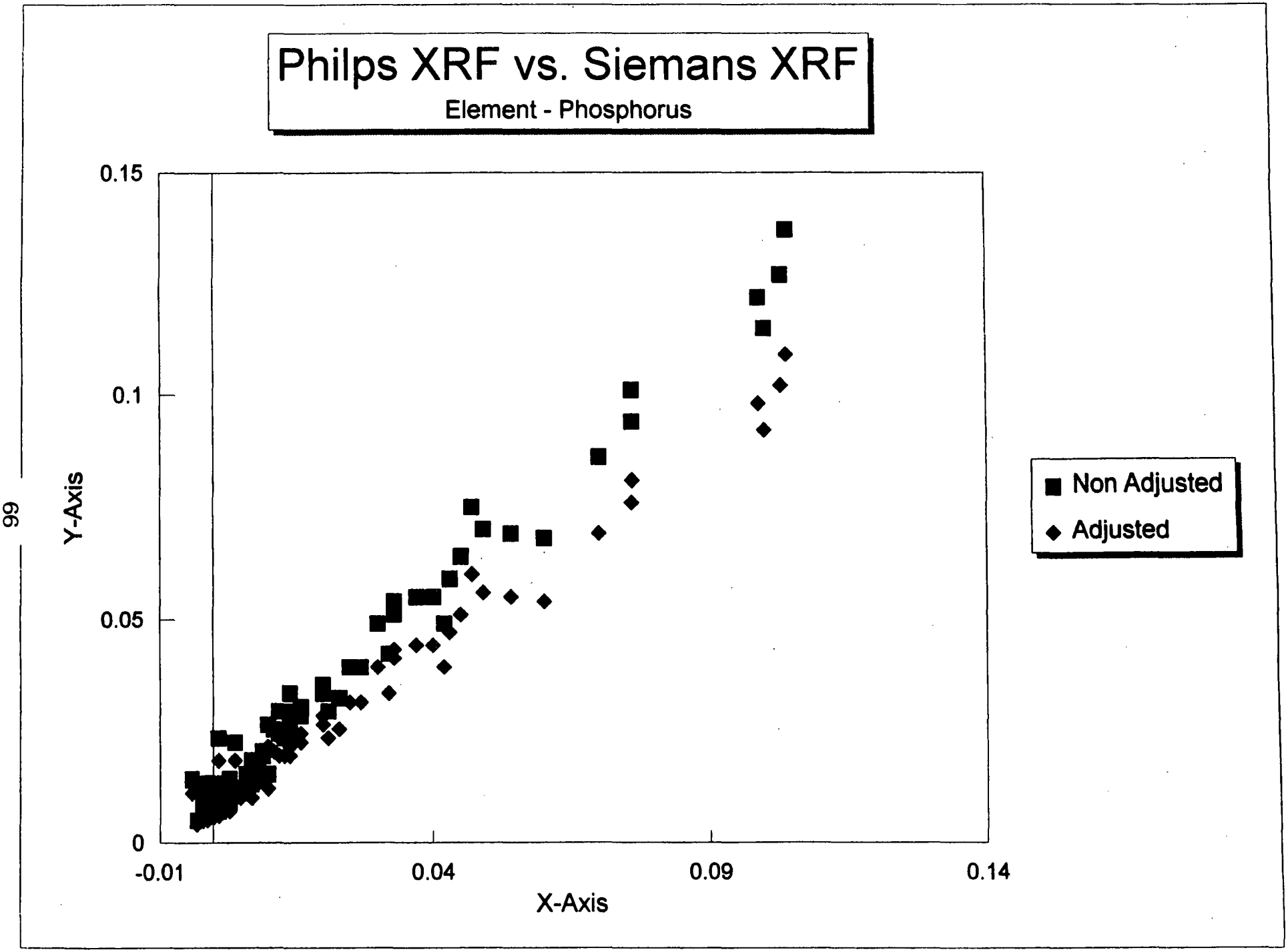
Wendell had completed the validation of the new XRF data before he left. I have just reproduced the data and summarized his work. Find attached a copy of the samples analyzed by the Philips XRF, Siemans XRF, and the Siemans data adjusted according to Wendell's analysis. Wendell adjusted the previous data by the following:

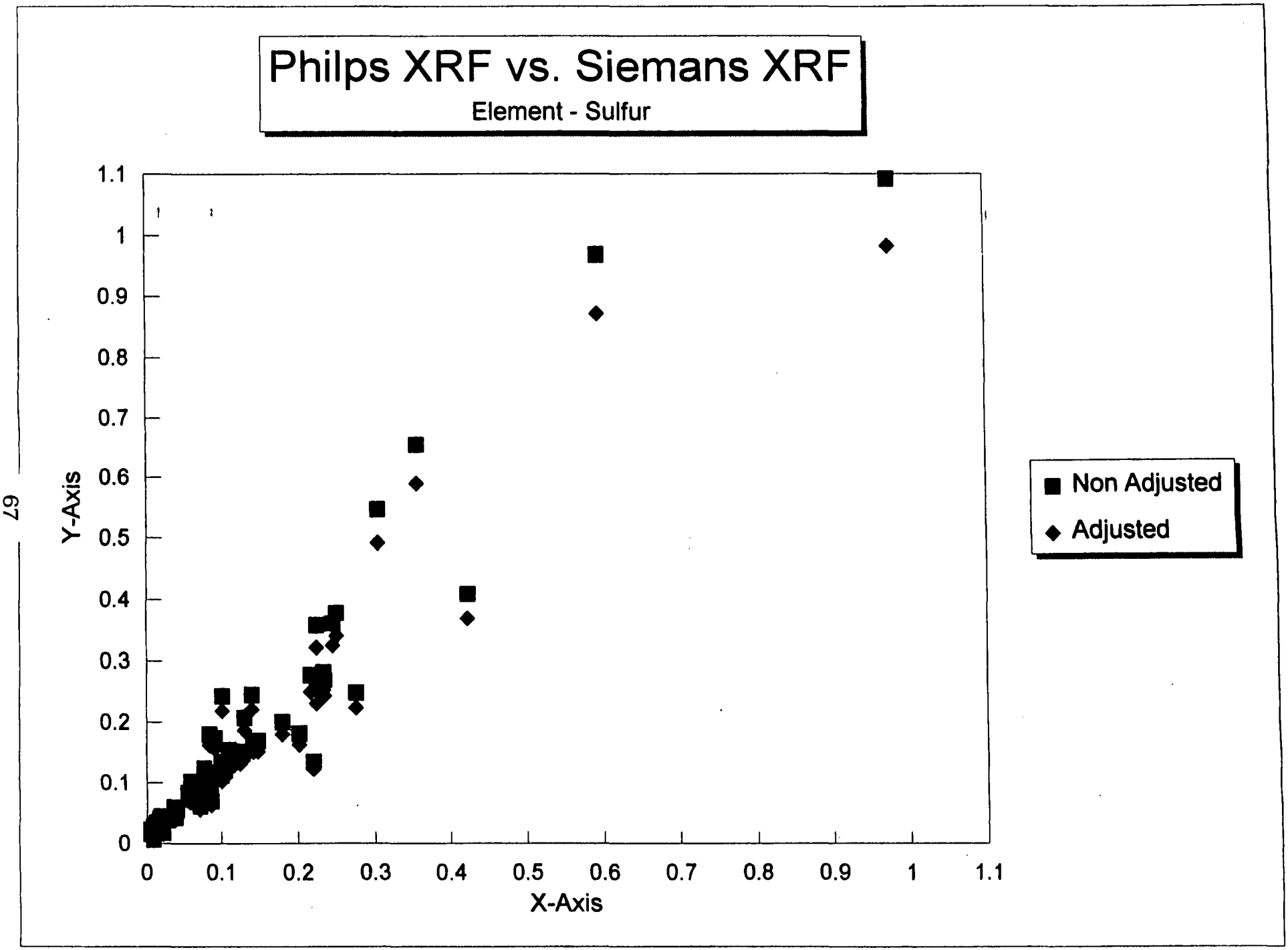
Strontium	× 0.92 =	Sr from Philips XRF
Manganese	× 0.90 =	Mn from Philips XRF
Phosphorus	× 0.80 =	P from Philips XRF
Sulfur	× 0.90 =	S from Philips XRF.

The previous data has been adjusted to match the Philips XRF, which has a higher intensity x-ray and better resolution.


Philps XRF vs. Siemans XRF
Element - Strontium
0.15
0.1
0.05
0
Y-Axis
0
0.05
0.1
0.15
X-Axis
Non Adjusted
Adjusted


Philps XRF vs. Siemans XRF
Element - Manganese
0.15
0.1
0.05
0
Y-Axis
0
0.05
0.1
0.15
X-Axis
Non Adjusted
Adjusted


Philps XRF vs. Siemans XRF
Element - Phosphorus
0.15
0.1
0.05
0
Y-Axis
-0.01
0.04
0.09
0.14
X-Axis
Non Adjusted
Adjusted


Philps XRF vs. Siemans XRF
Element - Sulfur
Y-Axis
X-Axis
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
Non Adjusted
Adjusted

Appendix 4 (TGA Calculations)

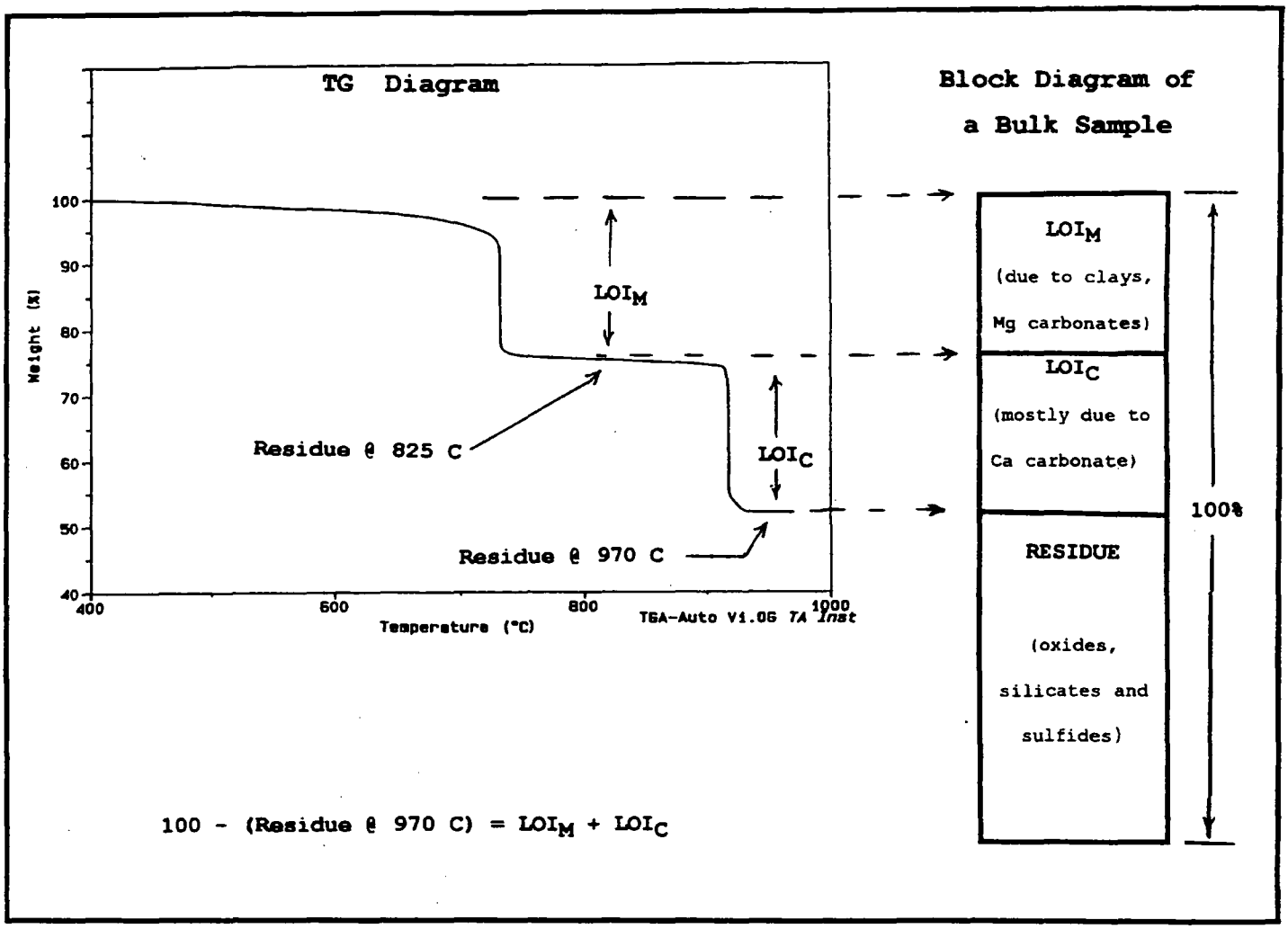
Updated TGA Calculations for Samples Containing Clay

The original TGA calculations for carbonate stones were developed using samples that contained very small amounts of clay. Hence, the calculations summarized in HR-337 [7], and reproduced in Illustration 1 below, produce poor estimates of Calcite and Dolomite contents for carbonate stones that contain a significant amount of clay. The updated calculations make several assumptions that can be summarized as follows: (1) the sample is fine enough that particle size effects can be ignored; (2) that Dolomite starts to decompose at temperatures above 550°C; and (3) that the Calcite decomposition temperature is above 910°C. All of these assumptions are oversimplifications of a very complex decomposition process that really merits selection of the decomposition temperatures on a sample by sample basis. Illustration 2 and the table below, summarize the appropriate thermal events and the basic steps in the calculations. The updated calculations typically improve the accuracy of estimating the Dolomite and Calcite content of samples prepared in the laboratory. This research program was limited to laboratory studies and no attempt was made to conduct testing on field samples. This particular aspect of the project would benefit from additional research to clarify certain issues that remain unresolved at the time that this report was drafted.

Example of Updated Carbonate Rock Calculations

Measured Data	value
Residue at 150 °C (moisture)	99.76
Residue at 550 °C (clay estimate)	98.43
Dolomite Decomposition Temp., °C	728
Residue @825 °C	76.60
Slope between 850 & 900 °C	0.053
Residue @900 °C	73.37
Calcite Decomposition Temp., °C	916
Residue @970 °C	56.18

Calculation Step	**Comments**	New Results		Old Results
1	calc LOIm = Residue@550-Residue@825	21.83		23.40
2	Convert to %MgCO3	41.82		44.83
3	Convert to moles MgCO3	0.4960		0.5317
4	calc LOIc = Residue@900-Residue@970	17.19		20.42
5	Convert to %CaCO3	39.09		46.44
6	Convert to moles CaCO3	0.3906		0.4640
7	Determine moles excess CaCO3	-0.1054		-0.0677
8	Convert MgCO3 to Dolomite	91.5	**Dolomite**	98.1
9	Convert moles excess to Calcite	0.0	**Calcite**	0.0
10	Insoluble = 100-Dolomite-Calcite	8.5	**Insoluble**	1.9



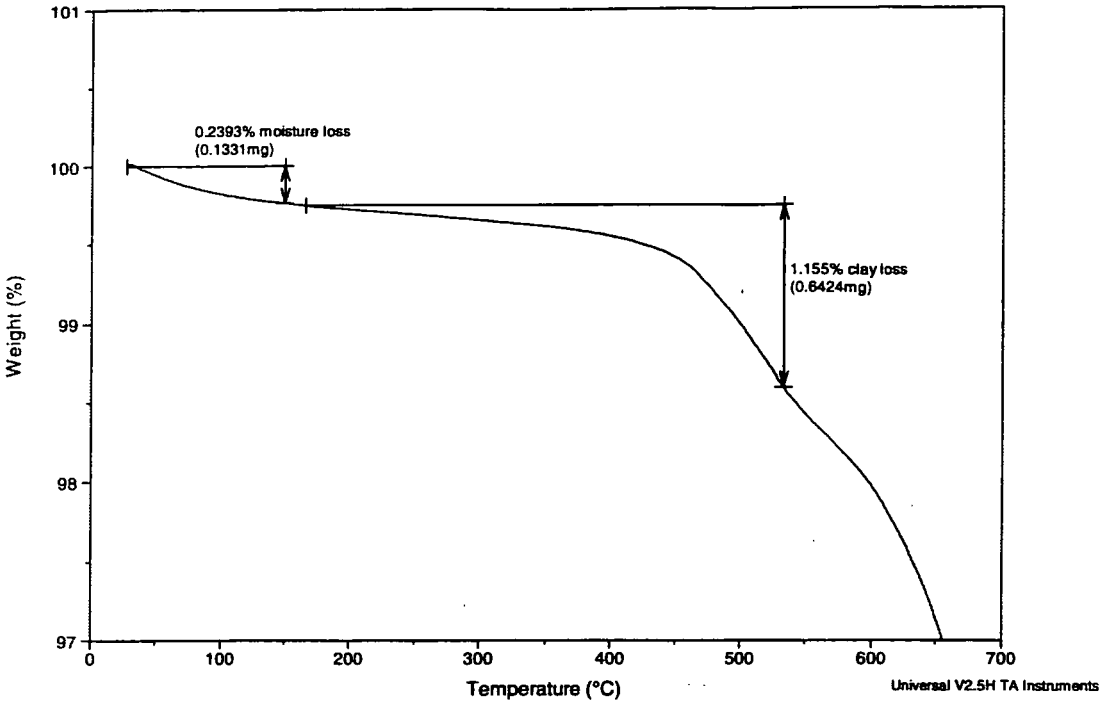
Calculation of Predicted compositions using TG results		
Step #	Description	Example
1	LOI_M = 100 - (Residue @ 825°C)	100 - 77.48 = 22.52
2	Convert to $MgCO_3$: LOI_M x 1.915928 = % $MgCO_3$	22.52 x 1.9159 = 43.15
3	Convert to moles $MgCO_3$: % $MgCO_3$ / 84.32 = moles $MgCO_3$	$43.15/84.32 = 0.5117$
4	LOI_C = (Residue @ 825°C) - (Residue @ 970°C)	77.48 - 53.12 = 24.36
5	Convert to $CaCO_3$: LOI_C x 2.274256 = % $CaCO_3$	24.36 x 2.274 = 55.40
6	Convert to moles $CaCO_3$: % $CaCO_3$ / 100.09 = moles $CaCO_3$	$55.40/100.09 = 0.5535$
7	Determine molar excess: moles $CaCO_3$ - moles $MgCO_3$ = excess $CaCO_3$	0.5535 - 0.5117 = 0.0418
8	Dolomite (%) = 2.187026 x % $MgCO_3$	43.15 x 2.187 = 94.4
9	Calcite (%) = moles excess $CaCO_3$ x 100.09	0.0418 x 100.09 = 4.2
10	Insoluble (%) = 100 - Dolomite - Calcite = 100 - (LOI_M x 1.9159) - (LOI_C x 2.274)	100 - 94.4 - 4.2 = 1.4

Illustration 1 – A diagram illustrating the original TGA carbonate calculations.

Sample: LAMONT MIX #3
Size: 55.6320 mg
Method: 40 degrees
Comment: In CO2 @ 100 ml/min

TGA

File: D:...\OLDTA files\Scott.093
Operator: J. Amenson
Run Date: 22-Apr-98 03:46



Sample: LAMONT MIX #3
Size: 55.6320 mg
Method: 40 degrees
Comment: In CO2 @ 100 ml/min

TGA

File: D:...\OLDTA files\Scott.093
Operator: J. Amenson
Run Date: 22-Apr-98 03:46